Kinetic and product studies for the oxidation of organic sulfides and sulfoxides in the presence of transition metal complexes

by

S. Sefa Köseoğlu

A thesis

presented to the Department of Chemistry

in partial fulfilment of the requirements

for the degree of

Master of Science

August 1980

Brock University

St. Catharines, Ontario

ABSTRACT

Rates and products of the oxidation of diphenyl sulfide, phenyl methyl sulfide, p-chlorophenyl methyl sulfide and diphenyl sulfoxide have been determined. Oxidants included t-BuO_2H alone, t-BuO_2H plus molybdenum or vanadium catalysts and the molybdenum peroxo complex $MoO(O_2)_2 \cdot HMPT$. Reactions were chiefly carried out in ethanol at temperatures ranging from 20° to 65°C.

Oxidation of diphenyl sulfide by t-BuO_2H in absolute ethanol at 65°C followed second-order kinetics with $k_2 = 5.61 \times 10^{-6}\ M^{-1}s^{-1}$, and yielded only diphenyl sulfoxide. The $Mo(CO)_6$-catalyzed reaction gave both the sulfoxide and the sulfone with consecutive third-order kinetics. Rate = $k_3[Mo][t\text{-}BuO_2H][Ph_2S] + k_3'[Mo][t\text{-}BuO_2H][Ph_2SO]$, where $\log k_3 = 12.62 - 18500/RT$, and $\log k_3' = 10.73 - 17400/RT$.

In the absence of diphenyl sulfide, diphenyl sulfoxide did not react with t-BuO_2H plus molybdenum catalysts, but was oxidized by t-BuO_2H-$VO(acac)_2$.

The uncatalyzed oxidation of phenyl methyl sulfide by t-BuO_2H in absolute ethanol at 65°C gave a second-order rate constant, $k = 3.48 \times 10^{-5}\ M^{-1}s^{-1}$. With added $Mo(CO)_6$, the product was mainly phenyl methyl sulfoxide; Rate = $k_3[Mo][t\text{-}BuO_2H][PhSCH_3]$ where $\log k_3 = 22.0 - 44500/RT$.

Both diphenyl sulfide and diphenyl sulfoxide react readily with the molybdenum peroxy complex, $MoO(O_2)_2 \cdot HMPT$ in absolute ethanol at 35°C, yielding diphenyl sulfone.

The observed features are mainly in agreement with the literature on metal ion-catalyzed oxidations of organic compounds by hydroperoxides. These indicate the formation of an active catalyst and the complexation of $t\text{-}BuO_2H$ with the catalyst. However, the relatively large difference between the activation energies for diphenyl sulfide and phenyl methyl sulfide, and the non-reactivity of diphenyl sulfoxide suggest the involvement of sulfide in the production of an active species.

To

İsmail and Handan Köseoğlu

and Ömer Erbölükbaşi

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to Professor R. R. Hiatt for his guidance and encouragement in every stage of this work and for the preparation of the computer programs.

I also extend my thanks to Mr. T. Jones for his assistance with NMR studies, to Mr. Ö. R. Köseoğlu for his assistance with lab work, and to Miss Janet Hastie for typing this thesis and for her great helpfulness.

Finally I would like to thank all faculty members of the Department of Chemistry for their valuable suggestions and their assistance in various ways.

Semih Sefa Köseoğlu

August 1980

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INTRODUCTION

Heterolytic Reactions of Peroxides

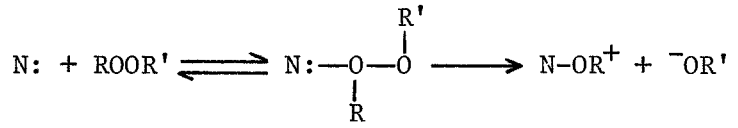
Hydroperoxides are known where the attachment of O-OH is to C, Si, Ge, Sn or S. However, compounds in which carbon is attached to O-OH, ROOH and $RC(=O)-O-OH$ are most commonly used and examined. Many papers have been written concerning the reactions of these compounds. There are at least ten reviews (1-10) and seven books dealing exclusively or partially with peroxides (11-17).

Free radical reactions are common in peroxide reactions. However, many reactions of peroxides proceed through polar mechanisms.

The earlier work for non-radical reactions of peroxides has been done by Swern (18). Excellent recent reviews have been covered by Swern (19). Also, there are some reviews by Edwards (1) and Bunton (20) who have reviewed the field with references through 1961. A particularly early study of the electrophilic behaviour of peroxides in reactions with electron pair donors has been done by Boeseken and Swern (21).

Reactions occur with a variety of peroxides with many types of substrates such as sulfides, sulfoxides, amines, hydroxylamines, olefins, phosphines and phosphites.

General characteristics and a proposed model have been given by J. O. Edwards (1) in the light of previous work.



On the basis of above model, the characteristics of the reaction should be as follows:

(a) Reaction should follow a second order rate law (first-order each in peroxides and in nucleophile).

(b) Reaction rate should be related to the basicity of the leaving group $R'O^-$.

(c) Definite orientation of reactants in T.S. should result in a negative value of $\Delta S^{\ddagger}$.

(d) Because of unshared electrons on the oxygen atom, the rate should be sensitive to acid catalysts.

All of the substrates previously mentioned are rapidly oxidized by peroxyacids. Smooth oxidations by hydroperoxides frequently requires a catalyst, however. Organic sulfides are an exception; oxidation to sulfoxides proceeds quite readily, so that the possibility of catalysis, other than by proton acids, has received little attention.

Oxidation of organic sulfides by peroxy acids, hydrogen peroxide and hydroperoxides

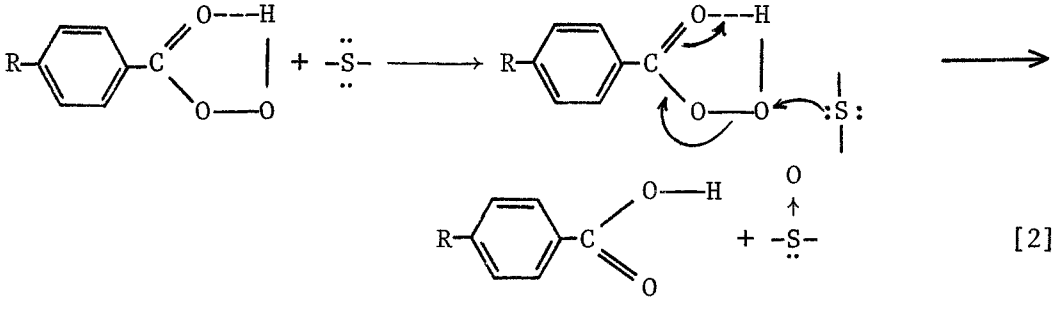
Reactions of organic sulfides with either hydrogen peroxide or hydroperoxides normally yield the sulfoxide whereas peracids readily produce sulfones. The rates of the oxidation of sulfide to sulfoxide

and sulfoxide to sulfone differ greatly. For example, peracetic acid in acetic acid oxidizes diphenyl sulfide to sulfoxide about a thousand times faster than the sulfoxide to sulfone (22). In contrast to the first stage of oxidation, there is little quantitative information about the second stage of oxidation. It is assumed that the same mechanism operates for it.

By Peroxy Acids

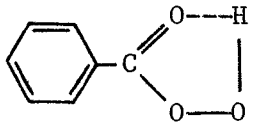
Overberger and Cummins (23) examined the oxidation of p,p'-dichlorobenzyl sulfide by peroxybenzoic acid and para substituted peroxybenzoic acids in toluene and isopropyl alcohol at -20 to -65°C.

They found the reaction to be first order in peroxyacid and first order in sulfide, with no apparent catalysis from the resulting benzoic acid. The reactions were characterized by low enthalpies of activation (5-11 kcal/mol) and large negative entropies of activation (-16 to -34 e.u.). Electron withdrawing substituents on the peroxyacid increased the rate, a Hammett plot giving $\rho = +0.91$. The authors suggested that the reaction occurs by a nucleophilic attack of a cyclic hydrogen bonded form of the peroxy acid by sulfide.

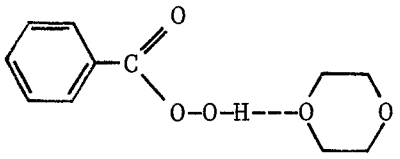


[2]

The oxidation proceeds faster in toluene than in isopropyl alcohol with lower energies and entropies of activation. Rate studies by Modena and coworkers (24-26) with peroxybenzoic acid in a variety of solvents ($CHCl_3$, CH_2Cl_2, CCl_4, benzene, nitrobenzene, DMF, dioxane, t-BuOH, i-PrOH, EtOH, MeOH, CF_3CH_2OH) demonstrated a rate increase with a change of solvent character from basic to non-basic solvents. There appears to be a general correlation of the rates with the capacity of peroxy acids to exist in either a chelate form (A) or an open-chain, solvated configuration (B).



A



B

The possibility of catalysis by strong acids seems to have been little explored. However, Modena and Todesco (24) do mention that presence of trifluoroacetic acid as a catalyst accelerates the reaction of diaryl sulfides with peroxybenzoic acid.

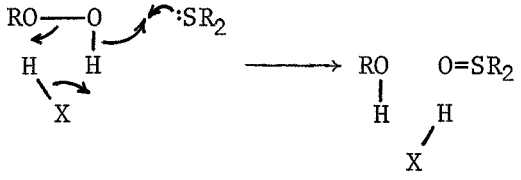
By hydrogen peroxide and hydroperoxides

The early mechanistic studies were performed by Bateman and coworkers (27-31) using both saturated and unsaturated sulfides with t-butyl and cyclohexenyl hydroperoxides. More recently, Curci and Edwards (32) have studied the reaction of H_2O_2 with thioxane.

In the hydroxylic solvents, the reaction is a second order overall, first order in both hydroperoxide (or H_2O_2) and sulfide. It is not retarded by free radical inhibitors, but is subject to acid catalysis. The stoichiometry is 1:1 as in equation 3.

$$R_2S + R'O_2H \longrightarrow R_2SO + R'OH \qquad [3]$$

Two mechanisms are offered to explain the above observations. The first (equation 4) consists of a one-step interaction of sulfide with hydroperoxide-solvent complex. The second (equations 5-7), involves an acid-base reaction between the peroxide and solvent with the resulting ion $ROOH_2^+$ as the active oxidant.



[4]

$$RO_2H + HX \rightleftharpoons ROOH_2^+ + X^- \qquad [5]$$

$$ROOH_2^+ + R_2S \longrightarrow ROH + R_2SOH^+ \qquad [6]$$

$$R_2SOH^+ + X^- \longrightarrow R_2SO + HX \qquad [7]$$

Both mechanisms require the catalytic effect of a solvent, which varies according to its acidity, or added acid which assumes the role of solvent HX. (See Tables 1 and 2.)

TABLE 1[a]

Oxidation of cyclohexyl methyl sulfide by hydroperoxides

	t-BuO_2H			cyclohexenyl-OOH		
Solvent	k^b	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$k^{b,c}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
t-BuOH	1.43×10^{-5}	16.9	-29	11.0×10^{-5}[b]	14.5	-32
n-BuOH	17.1×10^{-5}	14.4	-31			
MeOH	22×10^{-5}	13.5	-33	165.0×10^{-5}[b]	12.0	-34
Ethylene glycol	230×10^{-5}	12.1	-34	1270×10^{-5}[b]	10.4	-35
Benzene				560×10^{-5}[c]	10.9	
Cyclohexane				670×10^{-5}[c]	8.5	

[a] Data from reference 29.

[b] Second order rate constants at 50°C in $M^{-1}s^{-1}$.

[c] Third order rate constants at 50°C in $M^{-2}s^{-1}$.

TABLE 2[a]

Hydrogen Peroxide Oxidation of Thioxane and related Cases

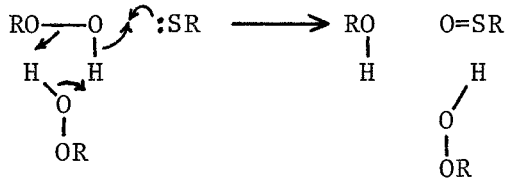
Solvent	$\Delta(k(H_2O)/k(solvent))$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
CH_3CO_2H	0.106	--	--
H_2O	1.000	13.0	-27
D_2O	1.68	12.9	-28
Ethylene glycol	5.20	13.6	-28
CH_3OH	41.8	14.5	-29
$2\text{-}C_3H_7OH$	226	15.3	-30
$t\text{-}C_4H_9OH$	473	17.4	-24
N-methyl acetamide	1170	18.7	-22

[a] Data from reference 32.

Evidence to support the first mechanism comes from comparison of cyclohexenyl hydroperoxide and t-butyl hydroperoxide in their reactions with cyclohexylmethyl sulfide under identical conditions. Cyclohexenyl hydroperoxide reacts faster than the t-butyl hydroperoxide (Table 1). It is also more acidic, and thus presumably less basic towards protonation by solvent. Stronger acidity should facilitate the reaction if the first mechanism is correct, while weaker basicity should disfavour the equilibrium of reaction 5. The large negative $\Delta S^{\ddagger}$ values (Tables 1 and 2) have been cited as favouring the cyclic first mechanism. However, the second mechanism, involving unstable ions requiring solvation could very well also have negative entropies of activation.

Not surprisingly, the oxidizability of sulfide is enhanced by electron donating groups and lowered by electron withdrawing groups (33).

In the non-hydroxylic solvents (30), the reaction is more complicated. In the simplest case, the role of solvent (HX) is assumed by a second molecule of hydroperoxide, and kinetically the reaction becomes second order with respect to hydroperoxide and first order with respect to sulfide.



[8]

It is regarded as a bimolecular interaction of the sulfide with dimeric hydroperoxide. The dimer is the dominant component in the neat hydroperoxide solution as has been mentioned by Bateman and Hughes (30) in their infrared studies.

In the absence of alternative hydrogen bonding substances such as alcohols, the weakly basic product sulfoxide forms a bond with hydroperoxide which causes a retarding effect on the rate of reaction. Also, other organic basis cause a retarding effect.

Addition of an acid stronger than the hydroperoxide changes the order of hydroperoxide from two to one.

Fractional orders (0.4-0.7) in sulfide concentration have been observed in some solvents and the reaction is subject to catalysis by oxygen. This behaviour has never been satisfactorially explained. In general, it seems best to stay away from non-hydroxylic solvents.

Metal catalyzed reactions of hydroperoxides

The metal catalyzed reactions of hydroperoxides may be divided into two classes which can be designated as homolytic or heterolytic.

The metal ion can cause homolytic decomposition of a hydroperoxide either through reductive or oxidative cleavage. Some metals, such as Co or Mn, can do both.

$$RO_2H + Co^{II} \longrightarrow Co^{III} + RO\cdot + OH^- \quad [9]$$

$$RO_2H + Co^{III} \longrightarrow Co^{II} + RO_2\cdot + H^+ \quad [10]$$

In other cases, catalytic activity depends on regeneration of the reductive ion. For example, mixtures of copper(II) and copper(I) catalytically reduce tert-amyl hydroperoxide in acetonitrile-acetic acid at 0°C (34). Copper(I) is regenerated *via* electron transfer oxidation of the ethyl radicals formed by the fragmentation of tert-amyloxy radicals.

$$CH_3CH_2C(CH_3)_2O_2H + Cu^I \longrightarrow Cu^{II}(OH) + CH_3CH_2C(CH_3)_2O\cdot \quad [11]$$

$$CH_3CH_2C(CH_3)_2O\cdot \longrightarrow (CH_3)_2CO + C_2H_5\cdot \quad [12]$$

$$C_2H_5\cdot + Cu^{II} \longrightarrow C_2H_4 + Cu^I + H^+ \quad [13]$$

Heterolytic reactions of hydroperoxides catalyzed by metal ions are distinguished from homolytic reactions in that no evidence exists for paramagnetic intermediates, products from β-scission of alkoxy radicals are not found, and product mixtures are generally simple. Rather few

metals, chromium, vanadium, molybdenum and tungsten, are effective. These, in their highest oxidation state (Cr^{VI}, V^{V}, Mo^{VI}, W^{VI}), as (frequently ill-defined) complexes, are sufficiently strong Lewis acids to complex the hydroperoxide (equation 14), reducing the electron density on the peroxidic oxygen, and permitting nucleophilic attack by a substrate (equation 15). Equally important, they are not such strong acids as to tear the hydroperoxide apart before the substrate gets there, as for example $AlCl_3$ or BF_3, nor are they strong one-electron oxidizing reagents.

$$M^n + RO_2H \underset{k_{-c}}{\overset{k_c}{\rightleftharpoons}} [M^nRO_2H] \qquad [14]$$

$$[M^nRO_2H] + S \xrightarrow{k_e} SO + ROH + M^n \qquad [15]$$

The homolytic reduction/oxidation (equations 16 and 17) does compete, but usually ineffectually.

$$[M^nRO_2H] \xrightarrow{k_d} M^{(n-1)} + RO_2\cdot + H^+ \qquad [16]$$

$$M^{(n-1)} + RO_2H \xrightarrow{\text{fast}} M^n + RO\cdot + HO^- \qquad [17]$$

In many respects, a hydroperoxide plus a suitable metal catalyst mimics the reactivity of a peroxyacid, epoxidizing olefins, oxidizing amines to amine oxides and sulfoxides to sulfones. Heterolytic oxidations which a hydroperoxide performs without catalysis, such as the

conversion of sulfides to sulfoxides or of phosphines to phosphine oxides are enormously accelerated by catalytic amounts of V^{V} o Mo^{VI}. (It should be mentioned that the metal ion need not be in its high oxidation state when added to the reaction medium. The hydroperoxide itself quickly performs that oxidation.)

Metal ion-catalyzed epoxidation of olefins

The synthetic utility of hydroperoxide-molybdenum (or vanadium) combinations, particularly with respect to oxidation of alkenes and alkynes has been recently reviewed by Sharpless and Verhoeven (35). The kinetic and mechanistic aspects have been discussed previously by Hiatt (36) and by Sheng and Zajacek (37).

The kinetics of epoxidation have been reported for 1- and 2-octene, and 2-methyl-1-pentene, in the presence of molybdenum hexacarbonyl (37, 38) and for cyclohexene with vanadium acetylacetonate (39). Also the substitution effects in aromatic systems was investigated by Howe and Hiatt (40) (Table 3).

Sheng and Zajacek (37, 38) have reported the effects of catalysts, solvent, temperature, olefin structure, hydroperoxide structure, oxygen, carbon monoxide and the stereochemistry for the reaction of 1- and 2-octene with p-nitrocumene, cumene and tertiary butyl hydroperoxides in the presence of molybdenum hexacarbonyl.

They have shown that molybdenum compounds, including oxides, sulfides, halides, salts, heteropolymolybdic acids, salts of heteropolymolybdic acids, esters of heteropolymolybdic acids, and molybdenum

coordination compounds are superior catalysts in these reactions. Reactions are slow below 90°C, but increase with increasing temperature.

Non-polar solvents such as benzene and methylcyclohexane are more effective solvents than polar solvents such as ethyl alcohol, and tertiary butyl alcohol. Low effectiveness of the polar solvent comes from competitive reaction between the solvent and the hydroperoxide for the molybdenum catalyst. Also the reaction rate increases with the more alkyl substituents on the double bond. The substitution of an electron withdrawing group in the para position of cumene hydroperoxide increases the rate of reaction. Presence of oxygen in the oxidation showed no effect on the rate, but it reduced the life of the catalyst. However, under the carbon monoxide atmosphere, the reaction rate is retarded due to the need to change at least one ligand by hydroperoxide. Another of their findings was the stereospecificity of the reaction. Pure cis- and trans-2-butene oxidation gave exclusively the corresponding cis- and trans- epoxides respectively.

The data obtained by Sheng and Zajacek indicate that epoxidation reaction proceeds according to the rate law:

$$\text{Rate} = k[t\text{-Bu}O_2H][\text{olefin}][Mo(Co)_6] \qquad [18]$$

Howe and Hiatt (40) also found this rate expression to apply for the epoxidation of styrene and some substituted styrenes with t-butyl hydroperoxide and molybdenum naphthanate (Table 3).

TABLE 3

Oxidation of olefins by t-BuO_2H in the presence of a metal catalyst

Styrenes[a]	Solvent	k_2[d] x $10^4 M^{-1}min^{-1}$	k_3[c] $L^{-2}M^{-2}s^{-1}$	Temp °C	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Catalyst
m-Cl	benzene	21.8		60°C			Mo(naphth)
p-Cl	benzene	30.5		60°C			Mo(naphth)
m-Br	benzene	26.1		60°C			Mo(naphth)
m-NO_2	benzene	31.0		60°C			Mo(naphth)
p-Me	benzene	3.10		60°C			Mo(naphth)
p-H	benzene	26.7		60°C			Mo(naphth)
cyclohexene[b]	cyclo-hexane	3.02		41.3	12.7	-19.8	$VO(acac)_2$
1-octene[c]			0.059	84.2	19.1	-14.2	$Mo(CO)_6$
			0.021	71.2			

[a] Data from reference 40.

[b] Data from reference 39.

[c] Data from references 37, 38.

[d] Rate = $k[M][RO_2H][substrate]$; $k_3 = k$; $k_2 = k[M]$.

On the other hand, in the epoxidation of cyclohexene by tertiary butyl hydroperoxide in the presence of vanadium acetylacetonate, Gould et al. (39) found first order dependence on cyclohexene and on catalyst, but the dependence on hydroperoxide concentration was analogous to the Michaelis-Menton equation for enzyme catalysis. The rate of epoxidation was retarded by tertiary-butyl alcohol which is a reaction product.

In contrast to molybdenum catalyzed oxidation, vanadium catalyzed oxidation showed a rapid catalyst deactivation. It appears that for epoxidation of olefins, molybdenum compounds are more active catalysts than vanadium compounds.

Metal catalyzed oxidation of amines

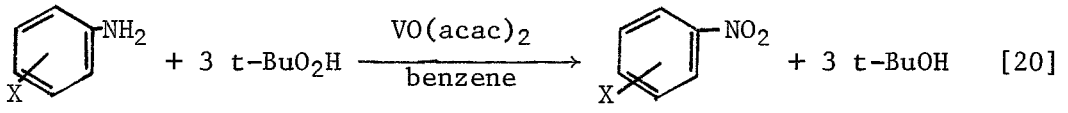
Sheng and Zajacek (41) have studied catalysis by groups VB and VIB transition metals of the oxidation of tertiary amines to amine oxides by hydroperoxides.

$$R^1\text{-}\overset{\overset{R^2}{|}}{N}\text{-}R^3 + ROOH \xrightarrow{cat.} R\text{-}\overset{\overset{R}{|}}{\underset{\underset{O}{\downarrow}}{N}}\text{-}R + ROH \qquad [19]$$

They found that vanadium is the most active species. Molybdenum also catalyzes the reaction, but it is less active than vanadium. Tungsten, niobium, tantalum, chromium, cobalt and manganese are poor catalysts. The relative reactivity of hydroperoxides was found to be t-amyl ≥ cumyl > t-butyl. Retardation of the rate by the alcoholic

solvents was interpreted a competitive complexing with catalyst and hydrogen bonding with the hydroperoxide.

Howe and Hiatt (42) have used $VO(acac)_2$ and t-BuO_2H to oxidize anilines to the corresponding nitrobenzenes.



[20]

The reaction is first order in aniline but suffers from auto-inhibition by t-BuOH and catalyst degradation. A Hammett plot obtained from initial rates gave a ρ-value of -1.63.

Metal ion catalyzed oxidation of phosphines, arsines, stibines

Oxidations of triphenylphosphine (43, 44), triphenyl arsine and triphenylstibine (45) by a hydroperoxide to their corresponding oxides is rapid, but can be made even faster by addition of catalytic amounts of molybdenum or vanadium compounds.

$$Ph_3P: + RO_2H \xrightarrow{V(naphth)} Ph_3PO + ROH \qquad [21]$$

$$\text{Rate} = [Ph_3P:][RO_2H](k_2 + k_3[V]) \qquad [22]$$

For triphenyl phosphine, it was found (44) that molybdenum naphthenate and $MoO_2(acac)_2$ were equally effective catalysts, while vanadium naphthenate was 1/10 as effective as the molybdenum compounds. n-Butyl hydroperoxide proved to be 10 times as reactive as t-butyl hydroperoxide.

The third-order rate constants for Ph_3P, Ph_3As and Ph_3Sb are shown in Table 4. It should be noted that while the reactions are all quite fast, they do not proceed at the same rate.

Metal ion catalyzed reactions of organic sulfides

Modena and coworkers (46, 47) have recently reported studies of the reaction of di-n-butyl sulfide with t-butyl hydroperoxide in dry ethanol at 25°C, catalyzed by dioxomolybdenum(VI) acetylacetonate (46) and by bisacetylacetonatooxovanadium(IV) (47). For individual reactions, the kinetics conform to a rate law which is first order with respect to sulfide, catalyst and hydroperoxide for both catalysts. However, the apparent rate constants are dependent on the initial concentration of hydroperoxide, and the data conform to a Michealis-Menton type rate law.

$$\text{Rate} = k[\text{cat}]_0[\text{t-BuO}_2\text{H}]/(k^1 + [\text{t-BuO}_2\text{H}]_0) \qquad [23]$$

where $k = k_{II}[\text{n-Bu}_2\text{S}]$.

No sensitivity towards free radical inhibitors or towards nitrogen *vs.* air atmosphere was observed. Also the reaction products did not retard the rate.

G. Modena *et al.* (48) have clarified the catalyst activation step, at least for $VO(acac)_2$. Both spectroscopic and potentiometric evidence indicates that in alcoholic solvents (ROH) and in the presence of t-butyl hydroperoxide, the oxoacetyl acetonate is rapidly oxidized and converted to a vanadate ester $VO(OR)_3$.

TABLE 4

The reaction of Group V nucleophile with t-BuO_2H and V naphthenate in ethanol.[a]

R_3M	k_3 (°C)[b] x $10^{-4}M^{-2}s^{-1}$	E_a (kcal mol^{-1})	log A
Ph_3P	1.0 (25)	11.2	7.8
Ph_3As	0.42 (35)	15.7	9.1
Ph_3Sb	2.7 (25)	9.7	6.7

[a] Data from references 44 and 45.

[b] Rate = $[Ph_3M][RO_2H](k_2 + k_3[V])$

It should be noted that while the reactions are all quite fast, they do not proceed at the same rate.

A mechanism for hydroperoxide-metal ion oxidation of nucleophiles

The previously cited workers are generally agreed on the basic features of the mechanism:

(1) An initial complexation of hydroperoxide with the metal ion species, on which electron and steric features of the R group have predictable effects.

$$RO_2H + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R\text{-}O\text{-}\overset{H}{\overset{|}{O}}\text{---}M \qquad [24]$$

(2) A competitive complexation by the solvent, or products, here denoted as ROH

$$ROH + M \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R\text{-}\overset{H}{\overset{|}{O}}\text{---}M \qquad [25]$$

(3) Rate determining attack by the nucleophile

$$R\text{-}\overset{H}{O}\text{-}O\text{---}M + N: \xrightarrow{k_3} R\text{-}\overset{H}{\overset{|}{O}}\text{---}M + N{\rightarrow}O \qquad [26]$$

The resulting rate expression has been most clearly outlined by Koshi (34).

$$-d[RO_2H]/dt = \frac{k_3[N:][RO_2H][M]}{K + (K_1/K_2)[ROH] + [RO_2H]} \qquad [27]$$

where $K_2 = k_{-2}/k_2$, $K_1 = k_{-1}/k_1$, and a steady state for concentration of

$R-O-\overset{H}{O}---M$ is assumed, so that $k_1K_1 = k_{-1} + k_3[N:]$. If $k_{-1} >> k_3$ and $[ROH] = [RO_2H]_0 - [RO_2H]$, it follows that

$$-d[RO_2H]/dt = \frac{k_3[N:][M]}{K_1/[RO_2H] + (K_1/K_2)[RO_2H]_0/[RO_2H] + (1 - K_1/K_2)} \quad [28]$$

Further simplification can be made if $K_1 \simeq K_2$

$$-\partial[RO_2H]/\partial t = \frac{k_3[N:][M][RO_2H]}{K_1 + (K_1/K_2)[RO_2H]_0} \quad [29]$$

This is the behaviour most often observed for catalysis by vanadium compounds. For molybdenum catalysis, where dependence on $[RO_2H]_0$ is usually not found, it is necessary only to point out that K_1 may easily be considerably larger than $(K_1/K_2)[RO_2H]_0$.

Objectives of this work

The similar reactivity of hydroperoxide-molybdenum or -vanadium combinations and organic peroxyacids has already been mentioned. Not surprisingly, an alternative mechanism has been advanced, that of an intermediate peroxymolybdic or peroxyvanadic acid--formed by reaction of hydroperoxides and metal complex--as the reactive species. The argument is not easily discounted, although peroxyvanadic and peroxymolybdic acids are known compounds and differ somewhat from hydroperoxide-metal ion in their reactivity towards substrates. Perhaps the most telling argument against is kinetic. If a metallic peroxyacid is the reactive

intermediate, it then follows that for the most reactive substrates, formation of the intermediate should be rate determining; structural changes in the substrate should not affect the rate of reaction. No such behaviour has been found. (Of course, for the phosphines, stibines and arsines, the necessary experiments have not been done. However, this group of highly reactive substrates forms a subclass for which it might be argued that given a reactive intermediate, surely Ph_3P, Ph_3Sb and Ph_3As should all react at the same rate. They do not.)

The reactive intermediate theory has recently been reactivated following on the isolation of a peroxomolybdenum complex, $MoO(O_2)_2 \cdot HMPT$* from reaction of H_2O_2 with MoO_3 (49, 50). The complex, unlike peroxymolybdic acid, quite closely parallels the reactivity of RO_2H-Mo with olefins (51, 52). Clearly, it has required further investigation.

The choice of organic sulfides and sulfoxides was based on the fact that of all the obvious substrates, these have been the least investigated. The previous work of Modena *et al.* (46, 47) was unsatisfactory in that structural effects were not treated, nor were sulfoxides as substrates given much consideration.

Thus the objectives: To establish a benchmark of reactivity/selectivity of RO_2H-Mo with respect to aryl sulfides and sulfoxides and to compare this with reactivity/selectivity of $MoO(O_2)_2 \cdot HMPT$.

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* Hexamethylphosphortriamide

EXPERIMENTAL

Materials used in this work and their purification steps

The sources of materials and their stated purity are shown in Table 5. The purities of diphenyl sulfide, diphenyl sulfoxide, diphenyl sulfone, phenyl methyl sulfide, phenyl methyl sulfoxide, phenyl methyl sulfone, p-chlorophenyl methyl sulfide, p-bromophenyl methyl sulfide, t-butyl alcohol, ethanol and 1,2-dichloroethane were checked by gas chromatography. In some cases UV and mass spectrometry were also used for this purpose.

The purity of t-BuO_2H was found by iodine titration. Compounds of molybdenum were used as obtained from commercial sources. Molybdenum hexacarbonyl was examined by mass spectroscopy, which showed the presence of tungsten hexacarbonyl and chromium hexacarbonyl as impurities. Sublimation under reduced pressure did not remove these impurities.

Instruments used in this work

For UV, GC and ^1H NMR analyses, 6 m Ebert grating and Cary-14 Ultra-visible spectrometers, F & M Laboratories 700 Gas chromatograph and Bruker WP-60 multinuclear fourier transform tuned for ^1H at 60 MHz with a sweep width of 750 Hz from TMS and A-60 NMR spectrometers were used respectively. Calculations were done using either the Wang 2200B or the Burroughs 6700 computers.

TABLE 5

Reagents purchased and used in the present work

Chemicals	Source	Purity a	Purity b
Diphenyl sulfide	Aldrich Chemicals		99
Diphenyl sulfoxide	Aldrich Chemicals	97	
Diphenyl sulfone	Aldrich Chemicals	97	
Thioanisole	Aldrich Chemicals		99
p-Bromothioanisole	Aldrich Chemicals	97	
p-Chlorothioanisole	Colombia Organic Chem.		99
Molybdenum hexacarbonyl	Alfa division	--	
Molybdenum naphthanate	ICN-K&K Laboratories	3% Mo (by weight)	
Molybdenum acetyl acetonate	ICN-K&K Laboratoreis	--	
Molybdenum trioxide	J. T. Baker Chemicals	100	
t-Butyl hydroperoxide	Lucidol division of Pennwalt Comp.		92.5
30% Hydrogen peroxide	BDH Chemicals	30	
Hexamethyl phosphoramide	Aldrich Chemicals	--	99
1,2-Dichloroethane	Aldrich Chemicals		100
t-Butyl alcohol	BDH Chemicals		100
Sodium iodide	BDH Chemicals	100	
Ethanol	Commercial	--	100

[a] as stated on the label

[b] as checked

Syntheses

Preparation of $MoO(O_2)_2 \cdot HMPT$

This diperoxo molybdenum complex was synthesized according to the procedure of Ozaki *et al.* (51). 50 g (0.348 mole) of molybdenum trioxide was suspended in 250 mL of 30% H_2O_2 with stirring at 40°C for 2 hours. Then the temperature of the bath was reduced to 10°C and 60 mL (62.3 g, 0.348 mole) HMPT was added dropwise to the solution which was stirred for two more hours. A yellow procipitate was filtered off, washed three times with ethyl ether and recrystallized from methanol solution at 40°C. It was stored under vacuum in a dark, cool place.

Preparation of phenyl methyl sulfoxide

Initially, C. R. Johnson's method (53) was used to synthesize thioanisoleoxide. The main problems in this method are the control of temperature, the composition of solvent which plays a quite important role in the solubility of $NaIO_4$ and $PhSCH_3$, and the tendency of the product to oxidize further.

Phenyl methyl sulfide (0.05 mole) was added to 0.0525 mole of sodium metaperiodate at 0°C in 110 mL of 50/50 (by volume) water and methanol mixture and the solution stirred overnight. The precipitated sodium iodate was removed by filtration, and filtrate was extracted with chloroform. The extract was dried over anhydrous magnesium sulfate. Finally, the solvent was removed under reduced pressure to get the products.

The ^1H NMR spectrum of product showed two main peaks; $PhSOCH_3$ and $PhSO_2CH_3$ at δ = 2.7 ppm and δ = 3.1 ppm, respectively.

Most preparations of phenyl methyl sulfoxide were done as follows: 25 mL of a 1.0 M solution of $PhSCH_3$ in EtOH, containing a small amount of molybdenum hexacarbonyl (9.83×10^{-3} mole) as a catalyst, was added into 100 mL round bottom flask with 1.0 M of t-BuO_2H in 25 mL EtOH. The solution was maintained at 35°C for approximately 1½ hours, while monitoring the disappearance of t-BuO_2H by iodometric titration. Removal of solvent from the mixture was done by vacuum distillation. Yields of the sulfoxide and the sulfone were 94% and 3% respectively.

Titrations

Two iodometric titration methods for t-BuO_2H were tried. Both of these methods are based on the reaction of the hydroperoxide with the iodide ion to produce iodine which can be titrated with sodium thiosulfate. The most commonly and conveniently used one is the "reflux" method (A). The other method (B) which has been used by Wibout and Van Leeuwen (54) is somewhat more discriminating than the reflux method in that it does not titrate hydroperoxide-carbonyl adducts.

Method A uses sodium iodide which is soluble in isopropanol-acetic acid mixture, provides good solubility conditions for organic compounds, and has the advantage of speed and lack of need for an inert atmosphere. In this method, oxygen in the solution is expelled by solvent vapour.

Method B uses potassium iodide in acetic acid at room temperature under a carbon dioxide atmosphere.

The Wibout method did not give consistent results in the presence of sulfur compounds so the "reflux" method was used for most of this work.

Rate studies

In ethanol:

Weighed amounts of catalyst ($Mo(CO)_6$, MoO_3 or $VO(acac)_2$) and the organic sulfide were added to a volumetric flask which was then filled with ethanol. A solution of t-BuO_2H was similarly prepared. Both flasks were equilibrated at reaction temperature for one hour before mixing aliquots to start the reaction.

Pre-mixing of the catalyst and organic sulfide seemed to be important. Pre-mixing of the catalyst with hydroperoxide, or no pre-mixing at all but rather preparation of three separate solutions, consistently gave slower and less reproducible reactions.

Mostly the reactions were followed for approximately 1½ hours at 35° or 65° C. Some reactions were done under Argon.

Samples (2 mL) were taken at 10 minute intervals. For reactions followed only by iodometric titration, a 500 µL aliquot was titrated immediately. For reactions followed by UV as well, the samples were quenched and stored in dry ice until the reaction was complete.

Preparation of samples for UV analysis

After bringing the sample to room temperature, 10 µL, or in some cases 20 µL, was added into 50 mL volumetric flask with Eppendorf Multivolume tip ejecting micropipet; then it was filled to the mark with ethanol.

Determination of extinction coefficients of diphenyl sulfide, diphenyl sulfoxide and diphenyl sulfone

A series of Ph_2S, Ph_2SO and Ph_2SO_2 stock solutions were prepared at different concentrations. Extinction coefficients for each compound were measured at 230, 235, 240, 245, 250, 255, 260, 265, 270 and 275 nm.

Measurement of optical densities in the UV region was determined at toom temperature in a quartz sample cell with a 10 mm path length within the cell compartment of a Cary-14 spectrometer.

After obtaining extinction coefficients, mixtures of Ph_2S, Ph_2SO and Ph_2SO_2 at known concentrations were prepared. Optical densities were measured at the 10 wavelengths for which extinction coefficients were calculated using a method for overdetermined simultaneous equations and compared to the known concentrations. The results are shown in Appendix 8.

These spectrometric parameters were measured also for the molybdenum peroxy complex and dichloroethane.

Treatment of concentrations vs time data

The data were fitted to a "model", i.e., the set of ordinary differential equations of the type $\partial[C_i]/\partial t = F(C_i, t)$, thought to best describe the reaction, using a Burroughs 6700 computer. The program employed a Gauss-Newton type of non-linear least squares routine, and a Runge-Kutta numerical integrator.

In $CDCl_3$

^1H Nuclear Magnetic Resonance spectral studies

^1H spectra were obtained for substituted phenylmethyl sulfides and their oxidation products, in $CDCl_3$ at 60 MHz in 5 mm tubes using a Bruker WP-60 FT NMR spectrometer at room temperature.

Preparation of samples

All NMR samples were prepared in two 5 mm NMR tubes, mixed quickly, and then replaced in the magnet of the spectrometer. One tube contained catalyst plus sulfide; the other contained t-butyl hydroperoxide. This mixing and replacement procedure took approximately two minutes.

The program used

A Bruker Automatic T1/II program in kinetics mode was used. Different numbers of scans and timing were employed for each experiment depending on the concentration of reactants, catalyst and temperature.

Interpretation of ^1H NMR spectra

Information obtained from ^1H NMR spectra of phenyl methyl sulfide, sulfoxide and sulfone showed that the peaks found at δ = 8.1-7.3 correspond to phenyl group hydrogens.

The methyl peaks of phenyl methyl sulfide, sulfoxide and sulfone are singlets at δ = 2.34, 2.71, 3.05 ppm respectively. The peaks are well-defined from each other, so increase or decrease in the intensity of peaks could be observed without any interference.

Gas chromatographic analyses

An F & M 700 Laboratory Gas Chromatograph which has thermo-conductivity detector, equipped with a Honeywell recorder having a disc integrator, was used to record the chromatograms. Generally ethanol was used as a solvent for the substances and 10 µl of sample solution was injected to determine the retention times of diphenyl sulfide, diphenyl sulfoxide, diphenyl sulfone, phenylmethyl sulfide, phenylmethyl sulfoxide and phenylmethyl sulfone.

Conditions in the determination of retention times of Ph_2S, Ph_2SO and Ph_2SO_2 (Chromatograms Appendix 4)

Column	6 feet, teflon
Packing	20% silicon rubber gum on Chromosorb W, 80-100 mesh
Column temperature	220°C
Injector temperature	210°C
Detector temperature	290°C
Carrier gas	Helium 100 mL/min

Retention times (min)

Ph_2S	2.33
Ph_2SO	5.27
Ph_2SO_2	5.79

Conditions in the determination of retention times of $PhSCH_3$, $PhSOCH_3$, and $PhSO_2CH_3$ (Chromatograms Appendix 4)

The same column was used for this case, but the conditions were different.

Column temperature	250°C
Injector temperature	210°C
Detector temperature	355°C
Carrier gas	Helium 100 mL/min

Retention times (min)

$PhSCH_3$	0.807
$PhSOCH_3$	1.397
$PhSO_2CH_3$	1.535

Conditions for runs #27 and #30

Column temperature	210°C
Injector temperature	205°C
Detector temperature	280°C
Carrier gas	Helium 100 mL/min
Filament current	150 mA

Under these conditions, the separation is reasonable for EtOH, sulfide and sulfoxide. But there is an overlapping between the sulfoxide and the sulfone peaks. This problem was eliminated by using the temperature programming during the separation of components. Unfortunately, another problem arose from the base line of chromatogram. This deviation of base line with change in oven temperature can be explained by the structure of thermocouple detector.

Gas chromatography was used to determine the concentration of each compound. Initially, calibration curves for diphenyl sulfide, diphenyl sulfoxide and diphenylsulfone were prepared by taking the known concentrations of each compound and recording their chromatograms. Graphs of concentration versus area of the peaks were linear.

This method of analysis was not useful sampling kinetic runs, however, for this case, because of the oxidation of sulfide to sulfoxide and sulfoxide to sulfone by unreacted t-BuO_2H proceded in the injection port. See Appendix 4 for results of 2 runs, #27 and #30 which were analyzed by titrations, UV and gas chromatography. UV and titrations gave the same results, but GC analysis consistently indicated a larger extent of reaction.

To eliminate this problem, Ph_3P was added to the samples to reduce t-BuO_2H to t-BuOH prior to GC injection. This method brought its own difficulty, that of eluting Ph_3PO and excess Ph_3P in a reasonable length of time and avoiding condensation of Ph_3PO in the detector block. This method was therefore not used. (A sample chromatogram is to be found in the appendices.)

RESULTS AND DISCUSSION

Oxidations of sulfides and sulfoxides by t-butyl hydroperoxide

Products of oxidation Experiments were carried out by Modena et al. (46, 47) and Hargrave (27, 28) to establish the stoicheiometry of both uncatalyzed and metal-catalyzed reactions of sulfides with t-butyl hydroperoxide. (In the following equations, C represents catalyst.)

$$t\text{-}BuO_2H + R_2S \xrightarrow{[C]} t\text{-}BuOH + R_2SO \qquad [30]$$

They have isolated the sulfoxide as a major product of the oxidation in 90% yield. This was confirmed with GLC. The other product is t-butyl alcohol which comes from the reduction of t-butyl hydroperoxide. No sulfone was observed either in protic or in aprotic solvents at the temperatures of 25°C, 45.9°C and 50°C.

$$R_2SO + t\text{-}BuO_2H \xrightarrow{[C]} R_2SO_2 + t\text{-}BuOH \qquad [31]$$

In this study, ultraviolet spectroscopy and titrations showed that the sulfoxide, the sulfone and t-butyl alcohol are the only products of oxidation. The stoicheiometry of oxidation has been confirmed by comparisons of the decrease in t-butyl hydroperoxide concentration (via titrations) versus the decrease in sulfide concentration and the

increases in sulfoxide and sulfone concentrations (via UV). Some typical data are given in Table 6.

In the absence of sulfide, solutions of t-BuO_2H + molybdenum catalyst showed no detectable loss of t-BuO_2H for periods of up to 2 hours at 35°C or 65°C.

Iodometric titrations of t-butyl hydroperoxide and GC analysis of the products have shown, in agreement with the observations made by Modena et al., that there are no extraneous products in these reactions. Some byproducts are seen in the reaction of the allylic sulfides with hydroperoxides (31). That is not the case in this work.

Selection of the catalyst and solvent

Preliminary work showed that absolute ethanol was capable of dissolving sufficient molybdenum hexacarbonyl, sulfides, sulfoxides, sulfones and t-butyl hydroperoxide.

Ethanol is a reasonable solvent for UV and GC. But on the other hand, it is a poor solvent for ^1H NMR studies, because its high concentration in the mixture prevents digital and manual integrations of methyl hydrogens of phenyl methyl sulfide, sulfoxide and sulfone. Therefore deuterated solvents were used, such as CD_3CN, C_6D_6 and $CDCl_3$. The most convenient and inexpensive solvent was $CDCl_3$ which provides very good solubility for the catalyst. In most of the NMR work for p-chloro, p-bromo substituted, and for phenyl methyl sulfide, $CDCl_3$ was used as a solvent.

TABLE 6

Data from a typical Mo-catalyzed reaction of diphenyl sulfide with t-BuO_2H.[a]

Time (min)	Concentrations t-BuO_2H[b]	Ph_2S[c]	Ph_2SO[c]	Ph_2SO_2[c]	Changes in Concentration $-\Delta$t-BuO_2H	$-\Delta Ph_2S$	ΔPh_2SO	ΔPh_2SO_2
0	0.8	0.4	0.0	0.0				
10	0.653	0.2322	0.1606	0.0072	0.1470	0.1678	0.1606	0.0072
20	0.59	0.1758	0.2134	0.0108	0.0630	0.0564	0.0528	0.0036
30	0.545	0.1413	0.2426	0.0161	0.0450	0.0345	0.0291	0.0053
40	0.512	0.1081	0.2689	0.0201	0.0330	0.0332	0.0263	0.0039
50	0.495	0.0947	0.2827	0.0226	0.0170	0.0135	0.0139	0.0025
60	0.477	0.0795	0.2936	0.0268	0.0180	0.0152	0.0109	0.0042
70	0.462	0.0678	0.3013	0.03090	0.0150	0.0117	0.0077	0.0041
80	0.452	0.0593	0.3094	0.0313	0.0100	0.0085	0.0081	0.0004
90	0.440	0.0417	0.3105	0.0378	0.0120	0.0076	0.0010	0.0065
100	0.429	0.0425	0.3173	0.0401	0.0110	0.0092	0.0069	0.0023

[a] 0.002 M $Mo(CO)_6$ in ethanol at 65°C.

[b,c] Mol L^{-1}. [b] By titration. [c] By UV.

An important aspect in the selection of catalyst for UV work was that it should not have an absorption in the region where sulfides, sulfoxides and sulfones have absorptions.

Absolute ethanol was the solvent chiefly used for reactions monitored by UV and titration, although hexane and 1,2-dichloroethane were explored.

The solubilities of several catalysts in three solvents and UV limits for the solvent are given in Table 7.

Purity of $Mo(CO)_6$

The purity of the molybdenum hexacarbonyl was checked by mass spectroscopy. It was shown to contain $W(CO)_6$ and $Cr(CO)_6$ as impurities. Reduced pressure sublimation did not remove these, probably because of their similar properties.

Atomic absorption analysis has shown that sublimed and unsublimed $Mo(CO)_6$ samples contain $Cr(CO)_6$ in 244 ppm and 148 ppm respectively. From relative mass spectrometric peak heights for W and Cr, the tungsten hexacarbonyl content was found to be 213 and 84.9 ppm for the sublimed and unsublimed molybdenum hexacarbonyl samples respectively.

Tungsten and chromium are known to be poor catalysts for the epoxidation of olefins (37). Their catalytic effects on the oxidation of sulfides and sulfoxides are not known, but would be expected to be similarly poor.

Therefore it seems safe to assume that these small amounts of W and Cr would not affect the rate of the reaction.

TABLE 7

Solubilities of several catalysts in, and UV limits of three solvents

	Solubilities[a]		
Catalyst	n-hexane	absolute ethanol	1,2-dichloroethane
molybdenum naphthenate	+	-	+
MoO_3	-	-	-
$Mo(CO)_6$	+	+	+
$MoO_2(acac)_2$	-	-	-
	UV limits		
lower limit	170	210	235 nm

[a] Based on visual observation of 0.01 g of the substance in 20 mL of solvent. "+" = no residual solid, "-" = residual solid.

Oxidation of diphenyl sulfide by t-butyl hydroperoxide

The uncatalyzed rate of t-butyl hydroperoxide consumption by diphenyl sulfide in absolute ethanol at 65°C was followed by iodometric titration (Table 8). The data (Figure 1) fit a second order rate law (Equation 32) with $k_2 = 5.61 \times 10^{-6}\ M^{-1}s^{-1}$.

$$\text{Rate} = k_2[RO_2H][Ph_2S] \qquad [32]$$

For the catalyzed reaction, MoO_3 was first used. Addition of amounts calculated to give an Mo^{VI} concentration of 1×10^{-2} M accelerated the reaction greatly, and produced both sulfoxide and sulfone (Figure 2). The obtained data fit the rate law which is shown in Equation 33

$$\text{Rate} = k_2[RO_2H][Ph_2S] + k_2'[RO_2H][Ph_2SO] \qquad [33]$$

where at 65°C, k_2/k_2' is about 30. But k_2 and k_2' turned out to be independent of the amount of MoO_3 added (Table 9) and upon closer inspection it was clear that not all of the MoO_3 had dissolved. Comparison with subsequent reactions using $Mo(CO)_6$ suggest that a saturated solution of MoO_3 in ethanol is about 5×10^{-4} M.

The $Mo(CO)_6$ catalyzed reaction of diphenyl sulfide with t-butyl hydroperoxide at 65°C gave similar results to those using MoO_3 except that rate constants were proportional to added catalyst (Equation 34).

TABLE 8

The uncatalyzed oxidation of diphenyl sulfide by t-BuO_2H at 65°C in ethanol

Time (min)	[t-BuO_2H][a]	[Ph_2S][a]	Plot[b,c]
0	0.8944	0.798	0.0
145	0.8555	--	0.0571
295	0.8193	--	0.1155
445	0.7817	--	0.1822
1405	0.6539	--	0.4714
1645	0.6194	--	0.5718

[b] $\ell n([R_2S]_0*[RO_2H]/([RO_2H]_0*([RO_2H] - ([RO_2H]_0 - [R_2S]_0)))/([RO_2H]_0 - [R_2S]))$

[c] $k_2 = 3.36 \times 10^{-4}\ M^{-1}min^{-1}$; r = 0.9985

[a] mol L^{-1}

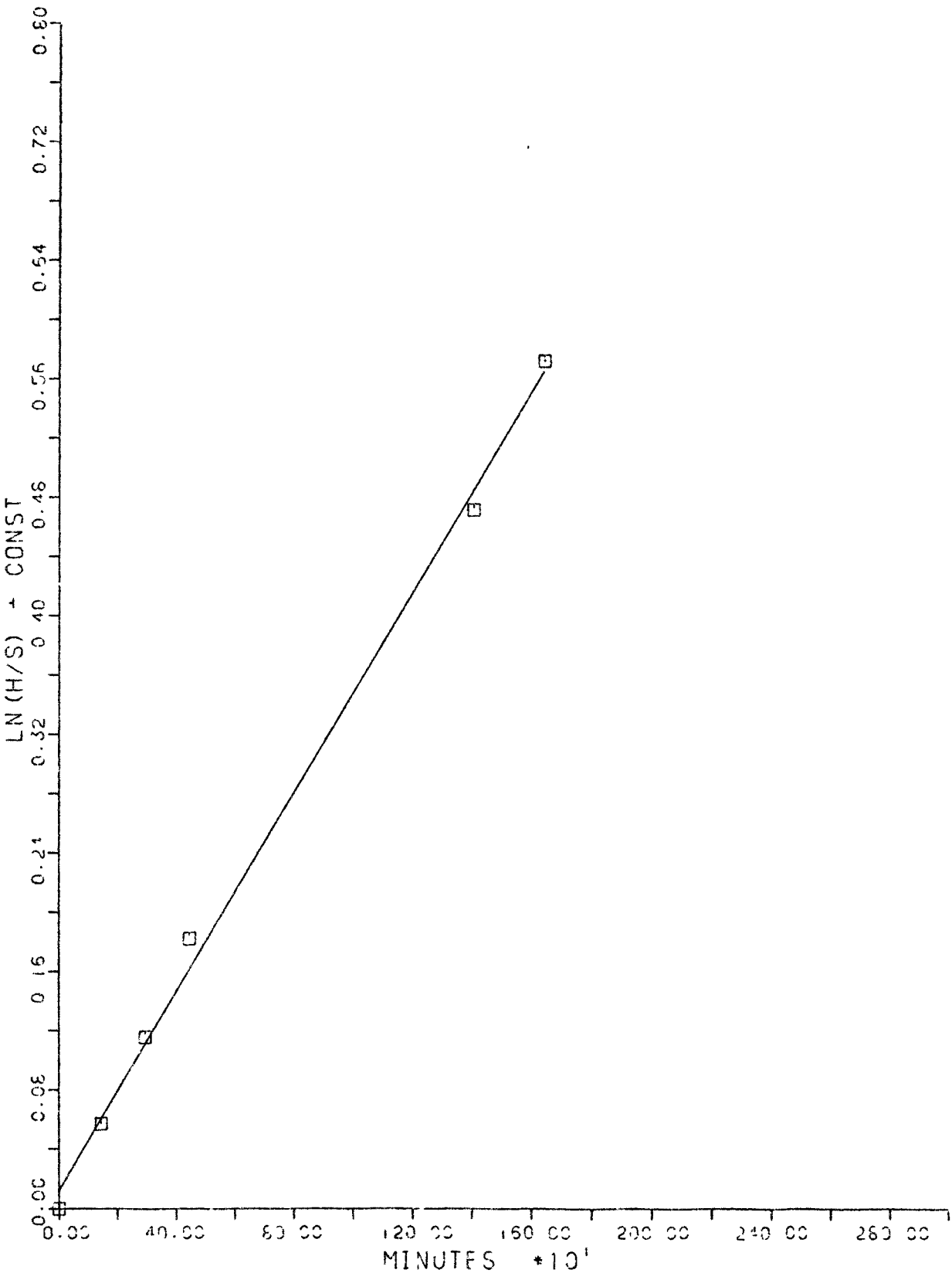


Fig. 1 Second-order rate plot for t-BuO_2H oxidation of diphenyl sulfide in ethanol at 65°C

TABLE 9

Reactions of diphenyl sulfide with t-BuO_2H catalyzed by MoO_3.[a]

Run No.	$[t\text{-}BuO_2H]_0$[b]	$[Ph_2S]_0$[b]	$[MoO_3]$[c]	k_2[d] x 10^2	k_2'[d] x 10^3
9	0.799	0.408	0.005	6.69	2.04
6	0.799	0.399	0.010	7.45	3.31
7	0.800	0.402	0.010	9.03	4.70
10	0.799	0.399	0.020	8.55	--
8	0.800	0.200	0.010	6.26	1.37
11	0.800	0.200	0.010	7.45	2.94

[a] At 65°C in ethanol

[b] $M\ L^{-1}$.

[c] $M\ L^{-1}$ as calculated if all added MoO_3 had dissolved.

[d] $M^{-1}min^{-1}$ from $-\partial[t\text{-}BuO_2H]/\partial t = k_2[t\text{-}BuO_2H][Ph_2S] + k_2'[t\text{-}BuO_2H][Ph_2SO]$

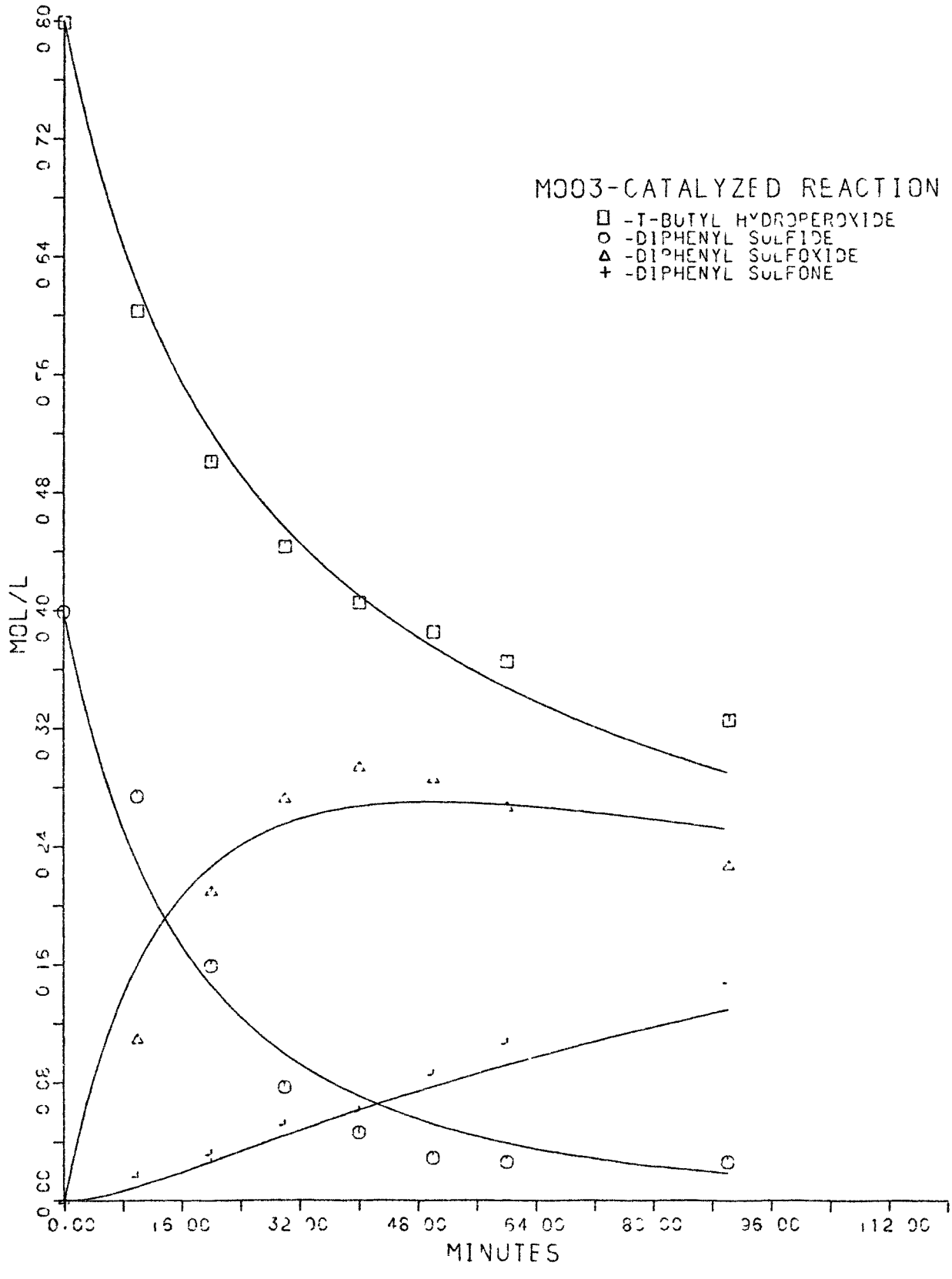


Fig. 2 Concentrations versus time of BuO_2H for the oxidation of diphenyl sulfide by t-BuO_2H in ethanol in the presence of MoO_3 at 65°C

$$\text{Rate} = k_3[Mo(CO)_6]_0[t\text{-}BuO_2H][Ph_2S] + k_3'[Mo(CO)_6]_0[BuO_2H][Ph_2SO] \quad [34]$$

The reaction was so fast, however, that a lower temperature seemed more appropriate. However at 35°C in ethanol, a problem developed. The reaction more often than not showed a strong oscillation in apparent (i.e., titratable) hydroperoxide concentration (Figure 3). This behaviour, while very interesting was not reproducible either in period or amplitude of the oscillations. It could be eliminated, however, by blanketing the reaction with argon (Figures 3, 4). All subsequent reactions of diphenyl sulfide were carried out under an argon atmosphere. The data are given in Table 10.

A plot of log k_3 versus 1/T gave an activation energy and A-factor for the first stage of the reaction (sulfide ⟶ sulfoxide) (Figure 5) of 18.5 kcal and $10^{12.6}$ respectively.

Oxidation of diphenyl sulfide by t-butyl hydroperoxide in the presence of either MoO_3 or $Mo(CO)_6$ gave both diphenyl sulfoxide and diphenyl sulfone. Diphenyl sulfone, however, is not very soluble in ethanol, and started to precipitate when conversion had reached about 10%, thus presenting analytical problems for rate studies beyond this point. Rather than change the analytical method, it was decided to study the second stage of the reaction in isolation, starting with diphenyl sulfoxide, rather than the sulfide.

A typical result is shown in Figure 6. Solutions of Ph_2SO, t-BuO_2H and a molybdenum catalyst in ethanol are quite stable, showing no

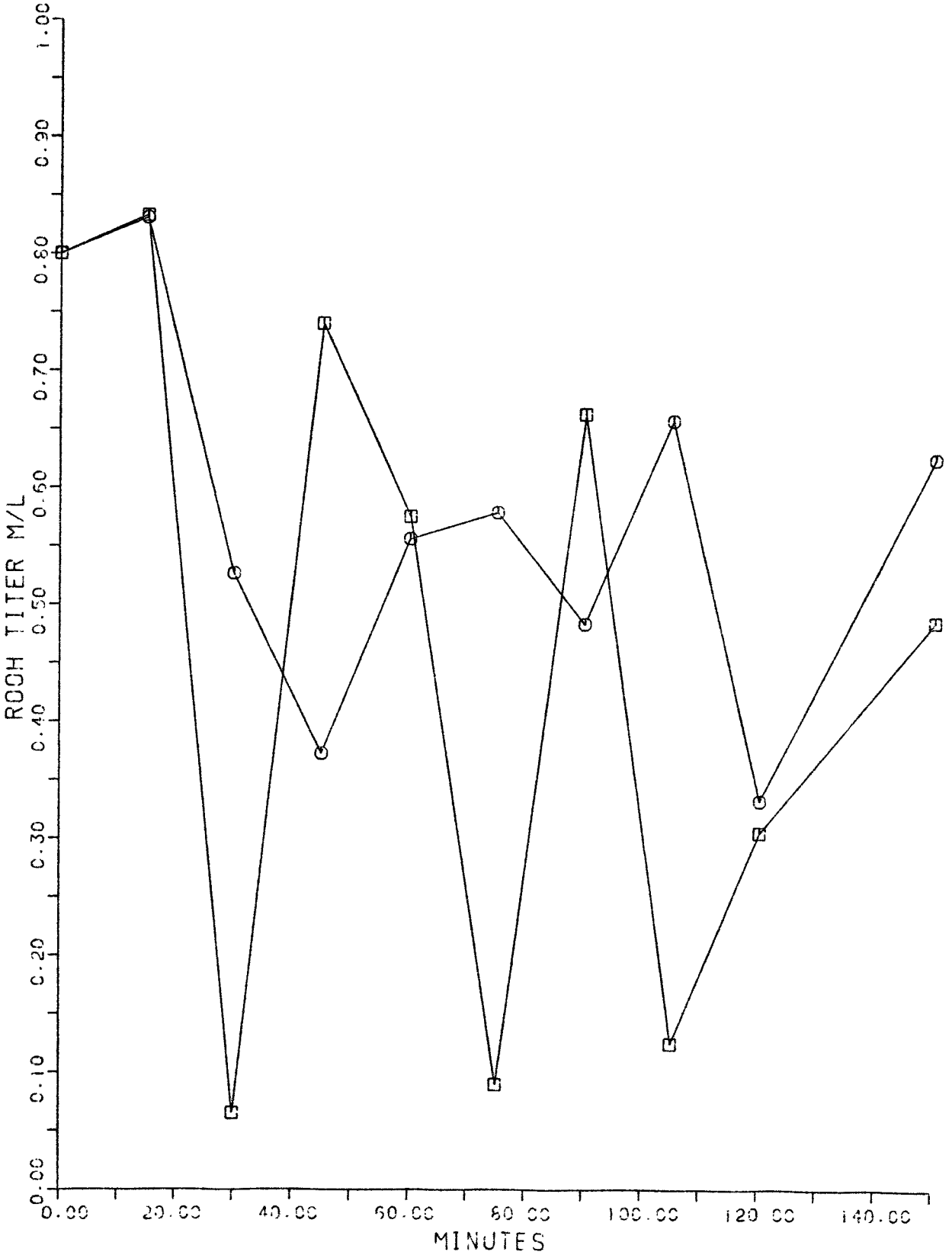


Fig. 3 Concentration of t-BuO_2H versus time for the oxidation of diphenyl sulfide at 35°C in ethanol under air in the presence of $Mo(CO)_6$ □ Run 19, o Run 20

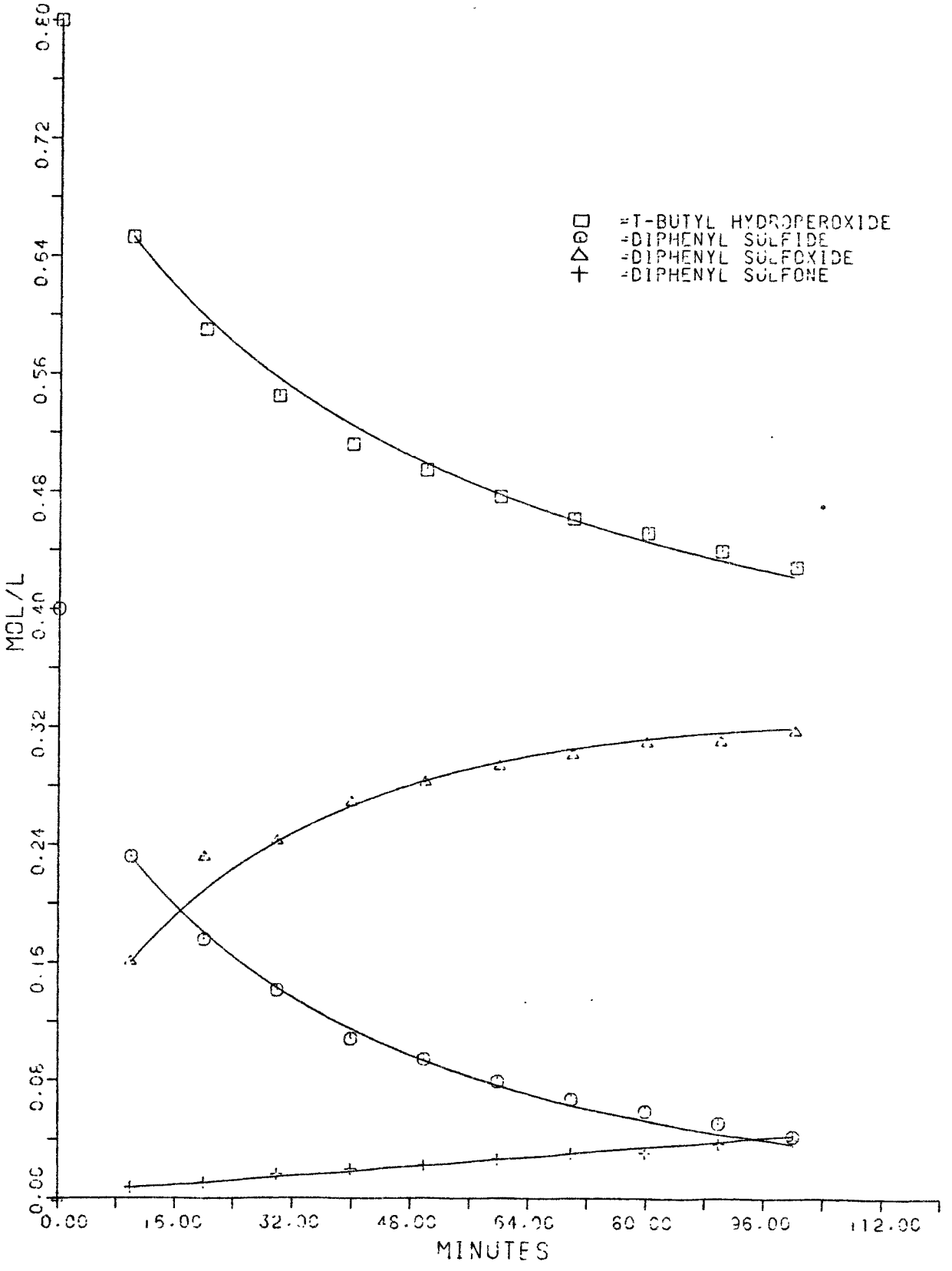


Fig. 4 Concentrations versus time for the oxidation of diphenyl sulfide by t-BuO_2H at 35°C in ethanol under argon atmosphere in the presence of $Mo(CO)_6$ (1.97×10^{-3} M)

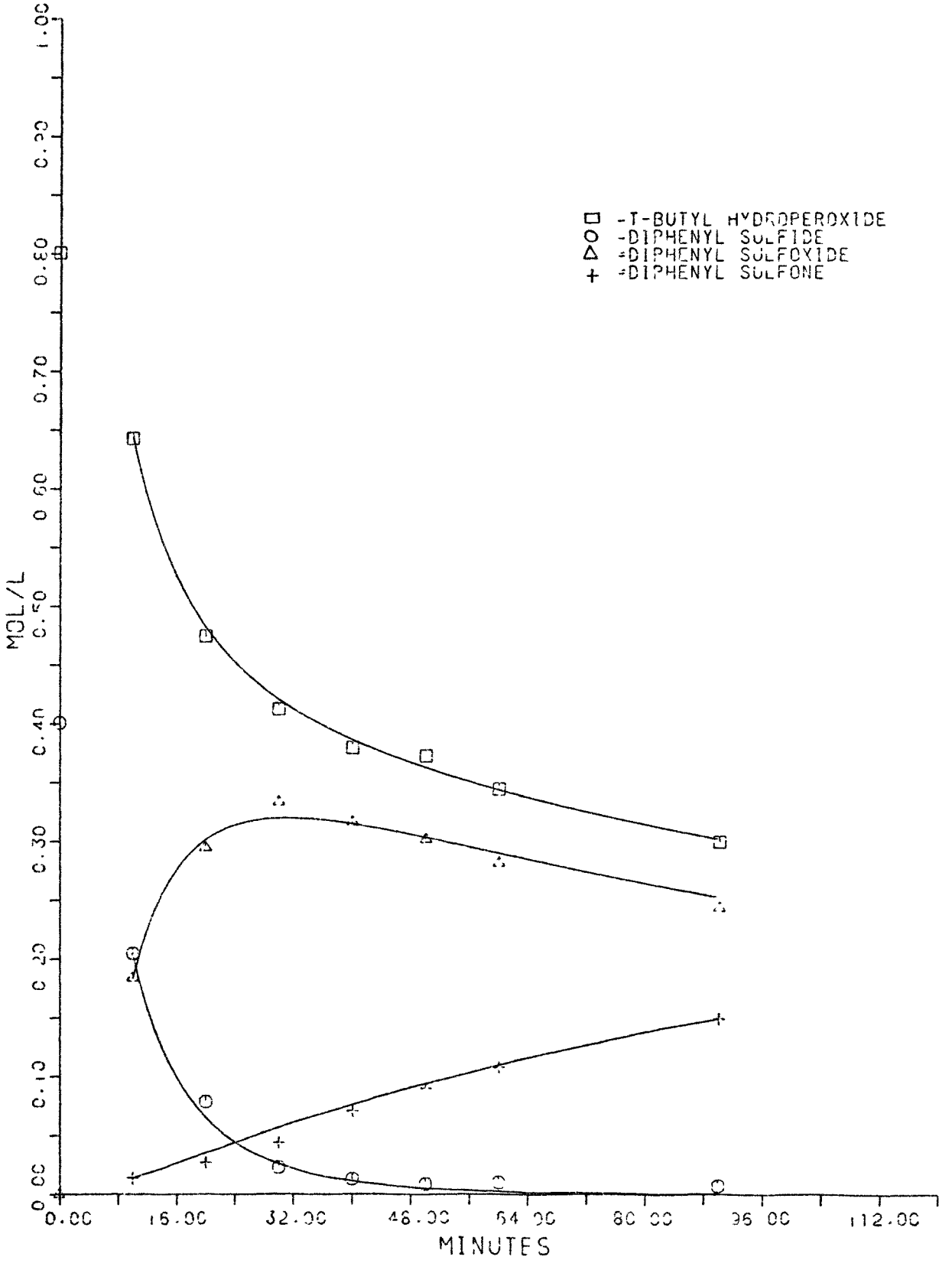


Fig. 4a **Concentrations versus time for the oxidation of diphenyl sulfide by t-BuO_2H at 65°C in ethanol under argon atmosphere in the presence of $Mo(CO)_6$ (8.9×10^{-4} M)**

TABLE 10

$Mo(CO)_6$-Catalyzed reactions of diphenyl sulfide with t-BuO_2H in ethanol.[a]

Run #	T °C	k_2[b] $M^{-1}min^{-1}$	k_2'[b] x 10^3	Variance[c] x 10^3	[Mo][d] x 10^3	k_3[e,f] $M^{-2}min^{-1}$	k_3'[e,f]
17	20	3.27	--	0.55	1.00	3.27	--
24	35	14.4	1.32	0.16	0.97	14.8	1.36
30	35	16.5	1.49	4.5	0.96	17.2	1.55
25	35	40.3	2.94	1.3	1.97	20.4	1.49
31	35	39.5	2.40	6.4	2.01	19.7	1.19
14[g]	65	208.2	15.2	1.2	0.895	237.6	17.4

[a] $[Ph_2S]_0$ = 0.400 M; $[t\text{-}BuO_2H]_0$ = 0.800 M; run under argon unless otherwise noted.

[b] From Rate = $k_2[RO_2H][R_2S] + k_2'[RO_2H][R_2SO]$

[c] Sum of squares, experimental - calculated values, for concentrations of t-BuO_2H, Ph_2S, Ph_2SO and Ph_2SO_2.

[d] Mol L^{-1}, calculated on added $Mo(CO)_6$.

[e] $k_3 = k_2/[Mo]$; $k_3' = k_3[Mo]$.

[f] Arrhenius plots for k_3, k_3' give
for k_3, E_a = 18.5 kcal mol^{-1}; log A = 12.62 ($M^{-2}s^{-1}$), r = 0.995
for k_3', E_a = 17.4 kcal mol^{-1}; log A = 10.73 ($M^{-2}s^{-1}$), r = 0.996.

[g] Run in air atmosphere.

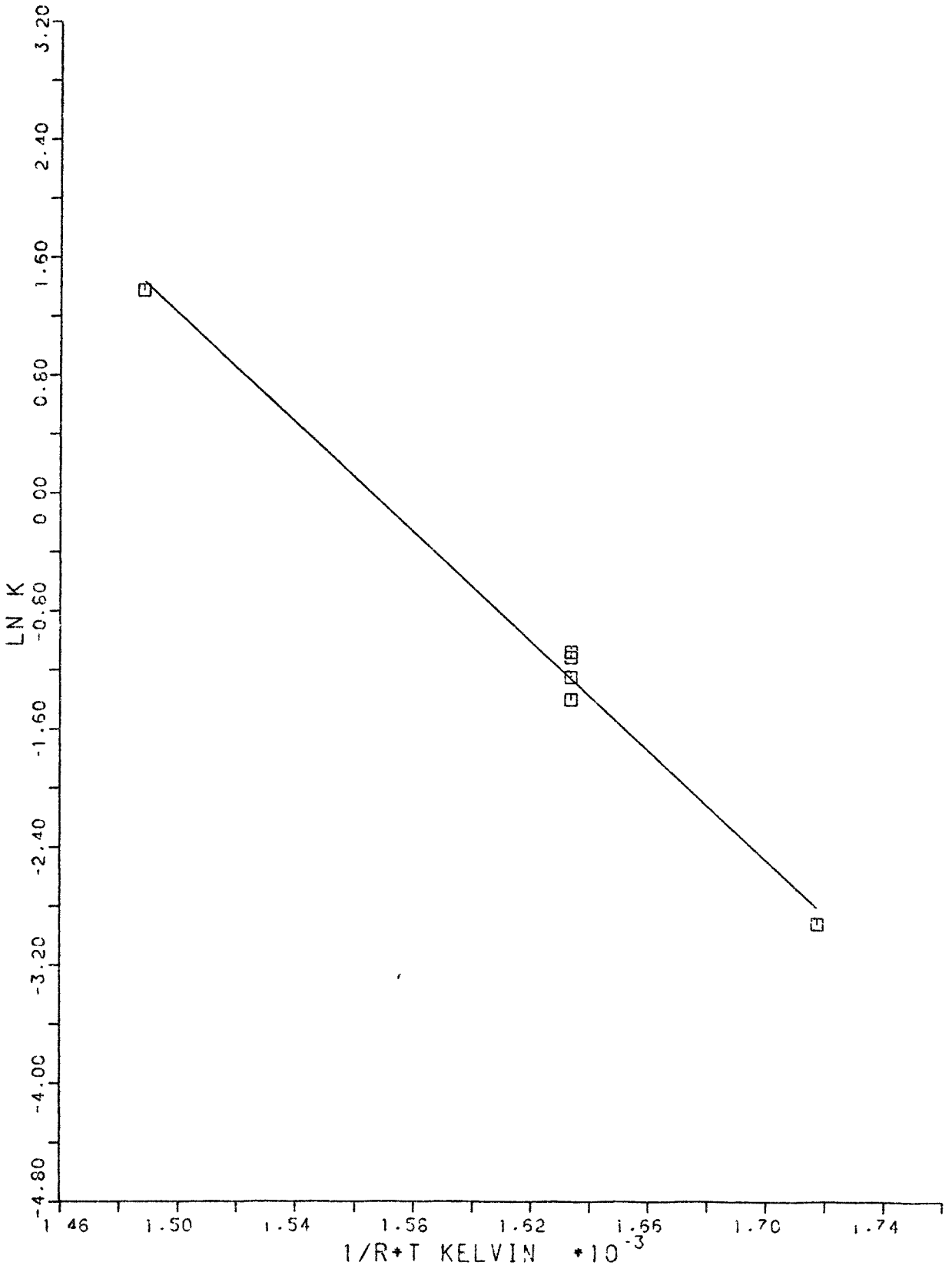


Fig. 5 Arrhenius plot for t-BuO_2H oxidation of diphenyl sulfide in ethanol and in the presence of $Mo(CO)_6$

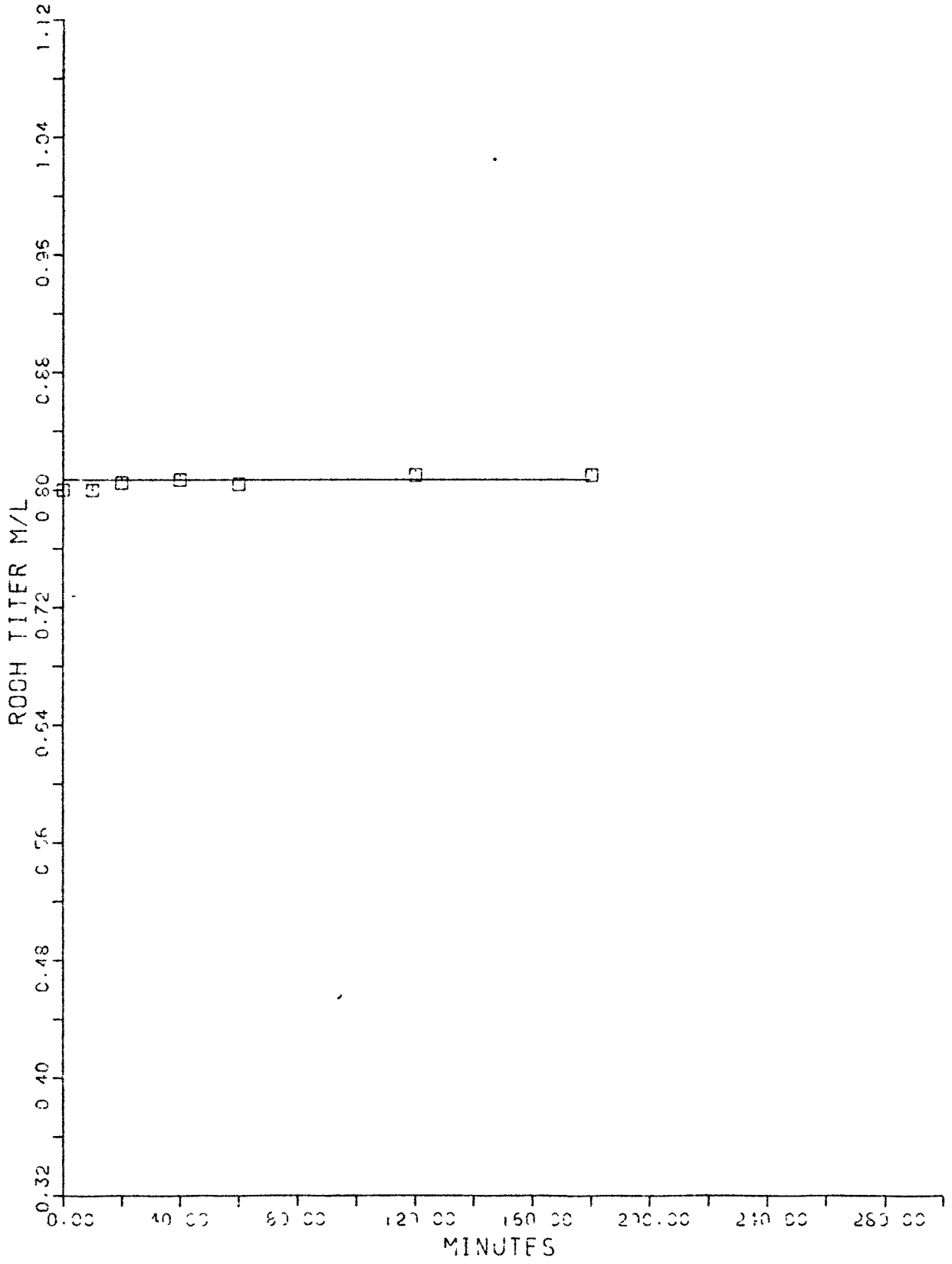


Fig. 6 Concentration of t-BuO_2H versus time for the reaction with diphenyl sulfoxide in the presence of $Mo(CO)_6$ at 35°C in ethanol

reaction for up to 3 hours! Conditions employed were 65°C, and either saturated MoO_3 or 0.02-0.001 M $Mo(CO)_6$. After 24 hours, there is a detectable loss of t-BuO_2H, but this may be due to free radical decomposition.

On the assumption that small amounts of the sulfide are required to somehow activate the catalyst, small amounts were added, to no effect. In a typical instance, with 0.4 M each of t-BuO_2H and Ph_2SO and 0.001 M $Mo(CO)_6$, Ph_2S sufficient to make its initial concentration 0.001 M. After 100 minutes of no reaction, the amount of Ph_2S was increased ten-fold. Still no reaction. Addition of Ph_2SO at the start of a Ph_2S reaction did not inhibit.

The conclusion seems to be that yes, Ph_2S is required, but in relatively large amounts, not small. The obvious alternative, that Ph_2SO is not the intermediate in conversion of Ph_2S to Ph_2SO_2 can be rejected by examination of the course of the Ph_2S + t-BuO_2H + Mo reaction (e.g., Figures 2 and 4). The relationship of Ph_2SO_2 production to Ph_2SO concentration is quite apparent. After all of the Ph_2S has been oxidized, the Ph_2SO concentration starts to drop and Ph_2SO_2 continues to increase. Computer modelling with $\partial[Ph_2SO_2]/\partial t = k[Mo][RO_2H][Ph_2SO]$ fits the data very well.

Since vanadium catalysts are reported (54) to work with sulfoxides, one experiment with $VO(acac)_2$ was tried. The conditions were 0.8 M t-BuO_2H, 0.2 M Ph_2SO, 0.004 M $VO(acac)_2$ in ethanol at 35°C in air. Since vanadium catalysts absorb strongly in the UV, the reaction was followed by titration alone, and a 1:1 stoicheiometry assumed. The reaction is

slow* (Figure 7), but gives a third order rate constant of 2.35 $M^{-2}min^{-1}$, about the same as for Ph_2S-activated Mo. Gc analysis of a parallel reaction after 335 minutes showed $[Ph_2SO_2]$ = 0.170 M. The rate constant gives $[Ph_2SO_2]$ at 335 minutes = 0.175 M.

Oxidation of phenyl methyl sulfide and substituted phenyl methyl sulfides

Reactions in $CDCl_3$

Still with the hope of using ^1H NMR analyses, attention was turned to phenyl methyl sulfides, where the methyl protons of sulfide, sulfoxide and sulfone are well separated singlets (Figure 8). Ideally, reactions could be run in an NMR tube, with periodic recording of peak intensities done automatically by the dedicated computer.

This, however, required a change of solvent, since the intensity of the ethanol protons overwhelmed the counting memory of the instrument. Reactions were therefore run in $CDCl_3$.

---

* As has been reported by Modena (46, 48) and Gould (39), addition of t-BuO_2H to the blue-green solution of $VO(acac)_2$ rapidly produces an intense red colour. Consequently an attempt was made to analyze mixtures of Ph_2S, Ph_2SO and Ph_2SO_2 by ^1H NMR. The aryl protons overlap considerably, but appear to fall into 3 separable regions (Appendix 6) which can be assigned to sulfone, sulfone + sulfoxide and sulfoxide + sulfide. In theory this is easily solvable. In practice, it didn't work possibly because for peaks with a lot of fine structure, the Bruker integrator is not always reliable.

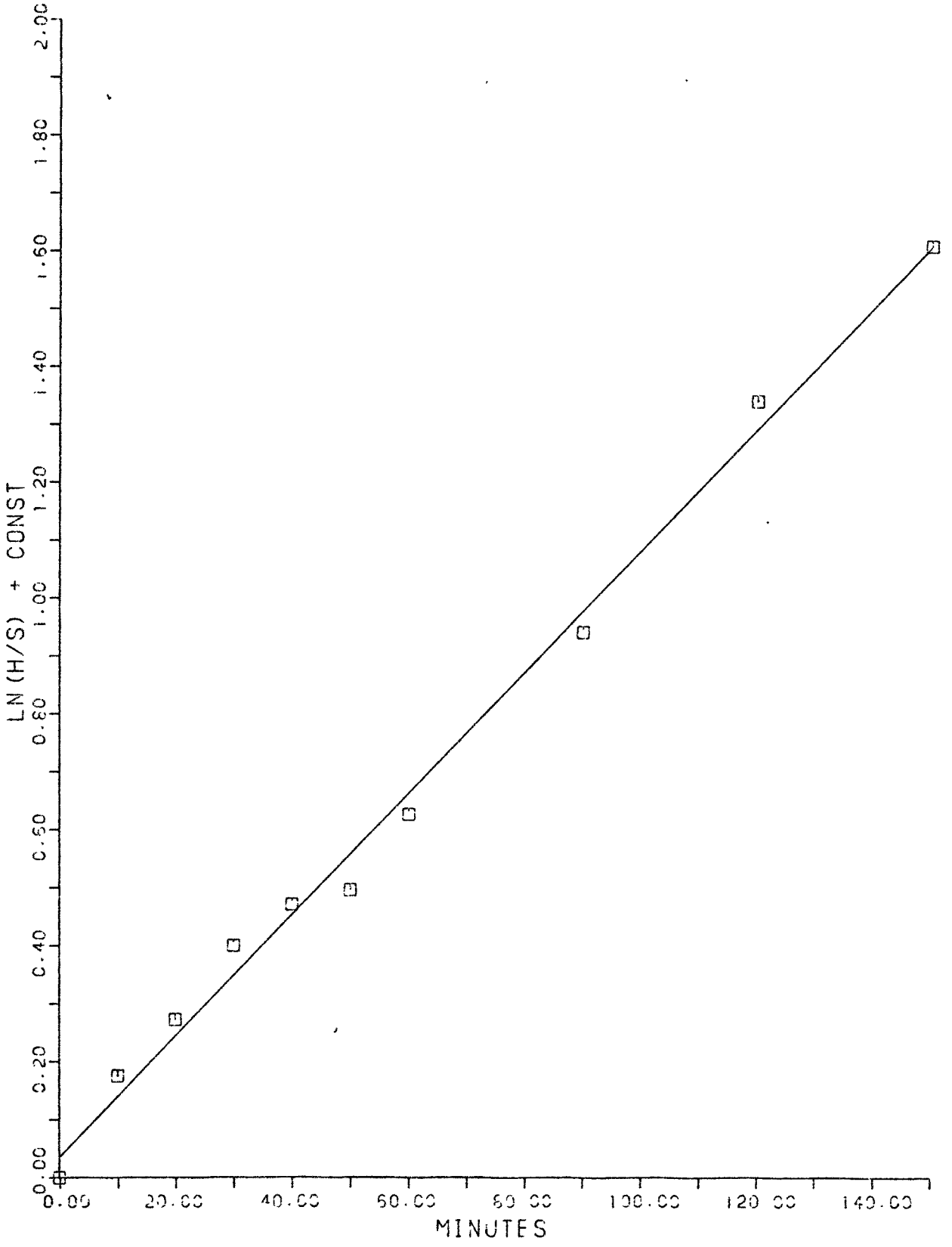
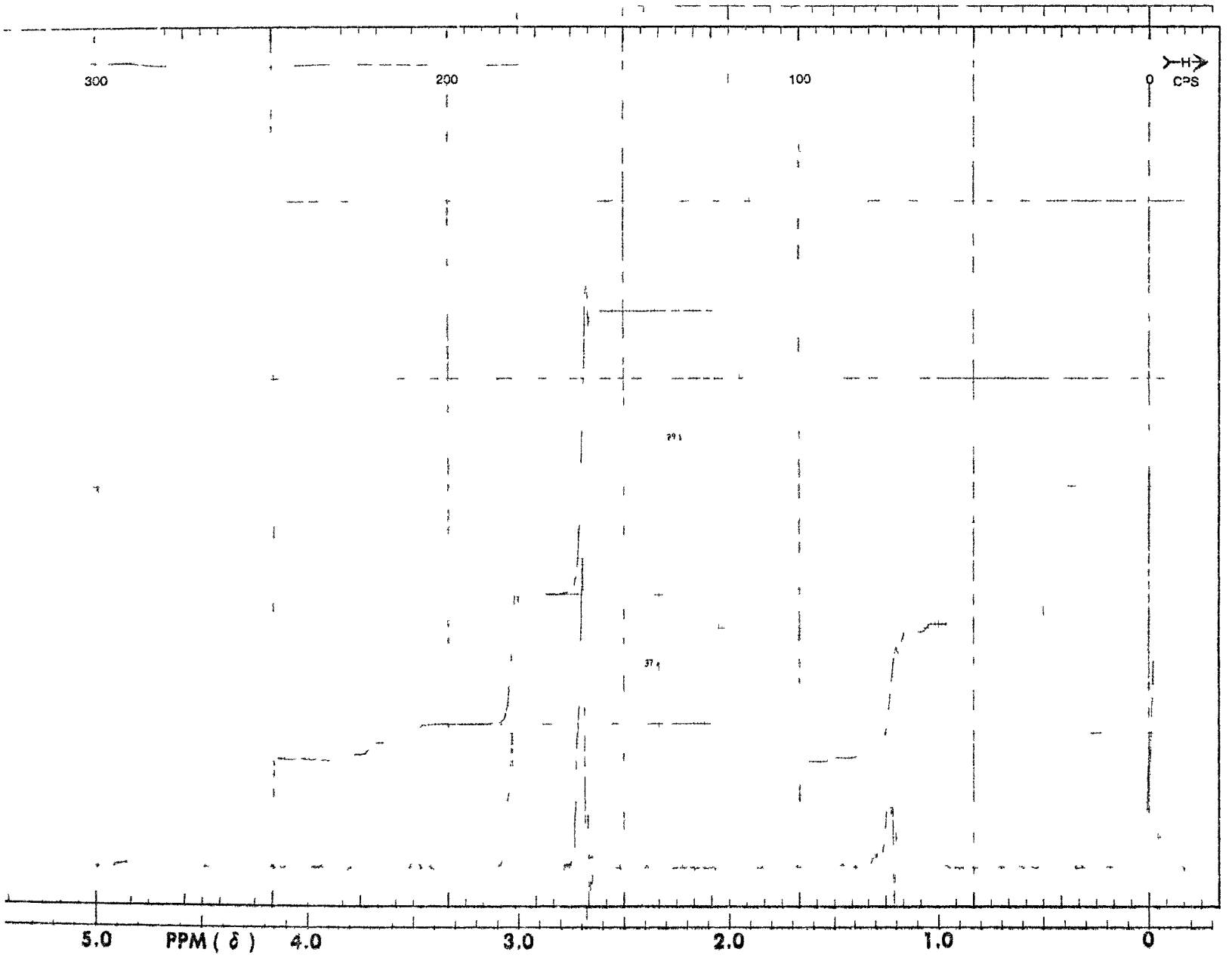


Fig. 7 Second-order rate plot for the reaction of t-BuO_2H with diphenyl sulfoxide at 35°C in ethanol in the presence of $VO(acac)_2$



60 MC NMR
SPECTRUM NO RUN #1

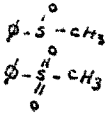
OPERATOR S. KOSSOGLUDATE

SAMPLE + ½ BuO_2H + $(Mn_{naph})_2$
in EtOH at 35°C

Sample was taken after 1370 min
22 ½ hours.

SOLVENT		$CDCl_3$	
TEMPERATURE		RT	°C
FILTER BANDWIDTH		4	cps
R F FIELD		.002	mG
SWEEP TIME		500	sec
SWEEP WIDTH		500	cps
SWEEP OFFSET		—	cps
SPECTRUM AMP		1/1.25	
INTEGRAL AMP.		10/4.0	

REMARKS:


.754 %

32.06 %

.272 ÷ 2.40 = .4

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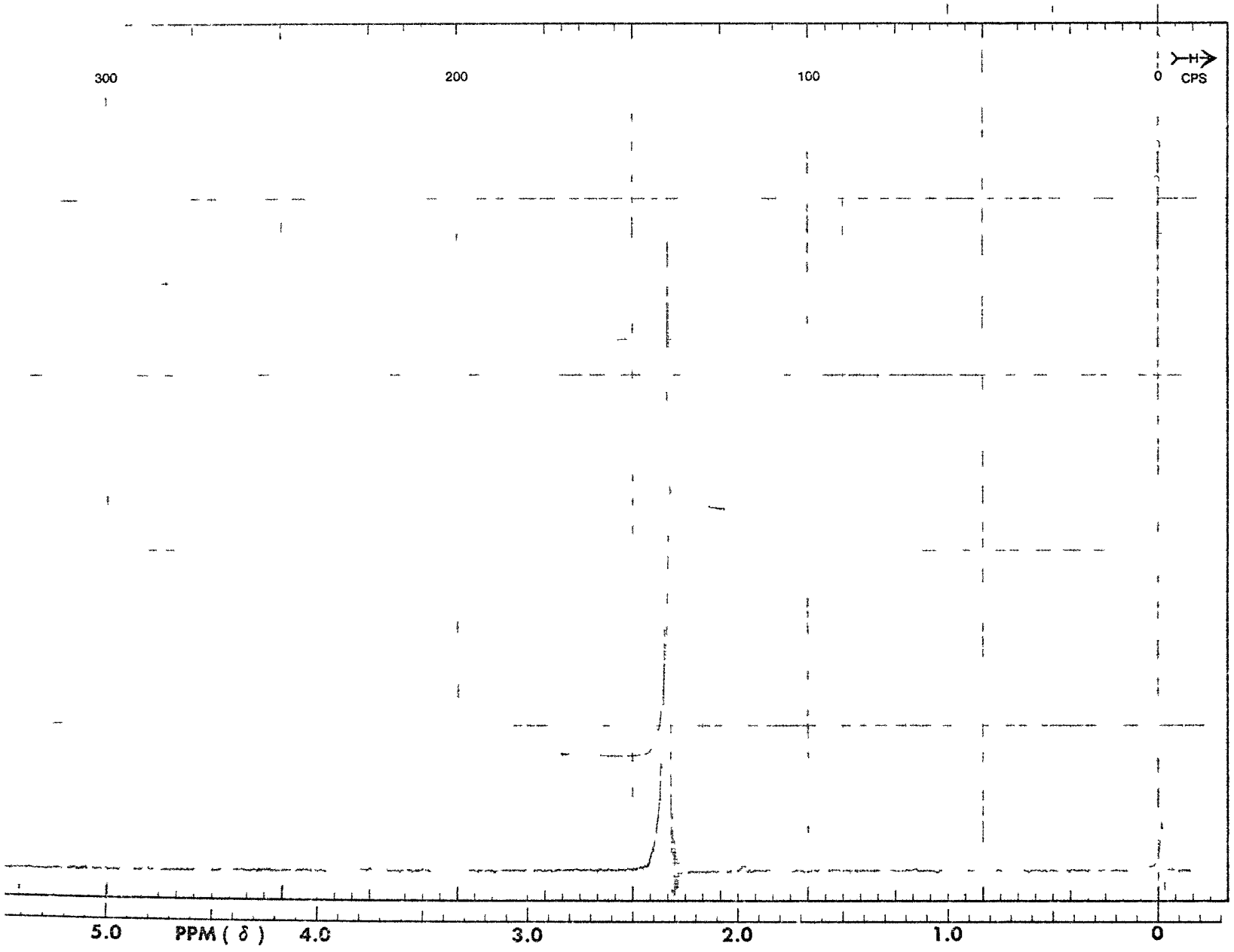
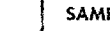
A-60, A-60a and D



60 MC NMR
SPECTRUM NO 3/329

OPERATOR S.KOSSOGLU DATE Nov. 17, 1979

SAMPLE 

SOLVENT	$CDCl_3$	
TEMPERATURE	R⁻	°C
FILTER BANDWIDTH	2	cps
R F FIELD	0 0 5	mG
SWEEP TIME	500	sec
SWEEP WIDTH	500	cps
SWEEP OFFSET	—	cps
SPECTRUM AMP	1/80	
INTEGRAL AMP	10/1.0	
REMARKS		

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A-60 A-60A and D

In a typical experiment, 1 M $PhSCH_3$ was oxidized by 2 M t-BuO_2H in the presence of 0.01 M $Mo(CO)_6$ at 30°C in an NMR tube, using ^1H peak intensities to monitor concentrations of the sulfur-containing species. A parallel run was carried out in $CHCl_3$ in a constant temperature bath, to obtain t-BuO_2H concentrations. The method appeared to work extremely well, individual runs giving excellent pseudo second order plots (Figure 9) and a number of runs were carried out, using p-chlorophenyl and p-bromophenyl methyl sulfides as well as the unsubstituted starting material.

Three features distinctly different from the reactions of diphenyl sulfide in ethanol emerged (1). The second stage, oxidation of phenyl methyl sulfoxides to phenyl methyl sulfones was so slow as to be a negligible consideration (2). Reactions at 20°C were less than 1/10 as fast as those at 30°C, suggesting either a very large activation energy, or undetected solubility problems of $Mo(CO)_6$ in $CDCl_3$ (3). The reactions were not reproducible, 2 runs under seemingly identical conditions giving rate constants differing by a factor of 2 or more.

Recalling difficulties encountered by earlier workers (29, 31) studying the uncatalyzed sulfide-hydroperoxide reaction in aprotic solvents, it was decided to abandon this line.

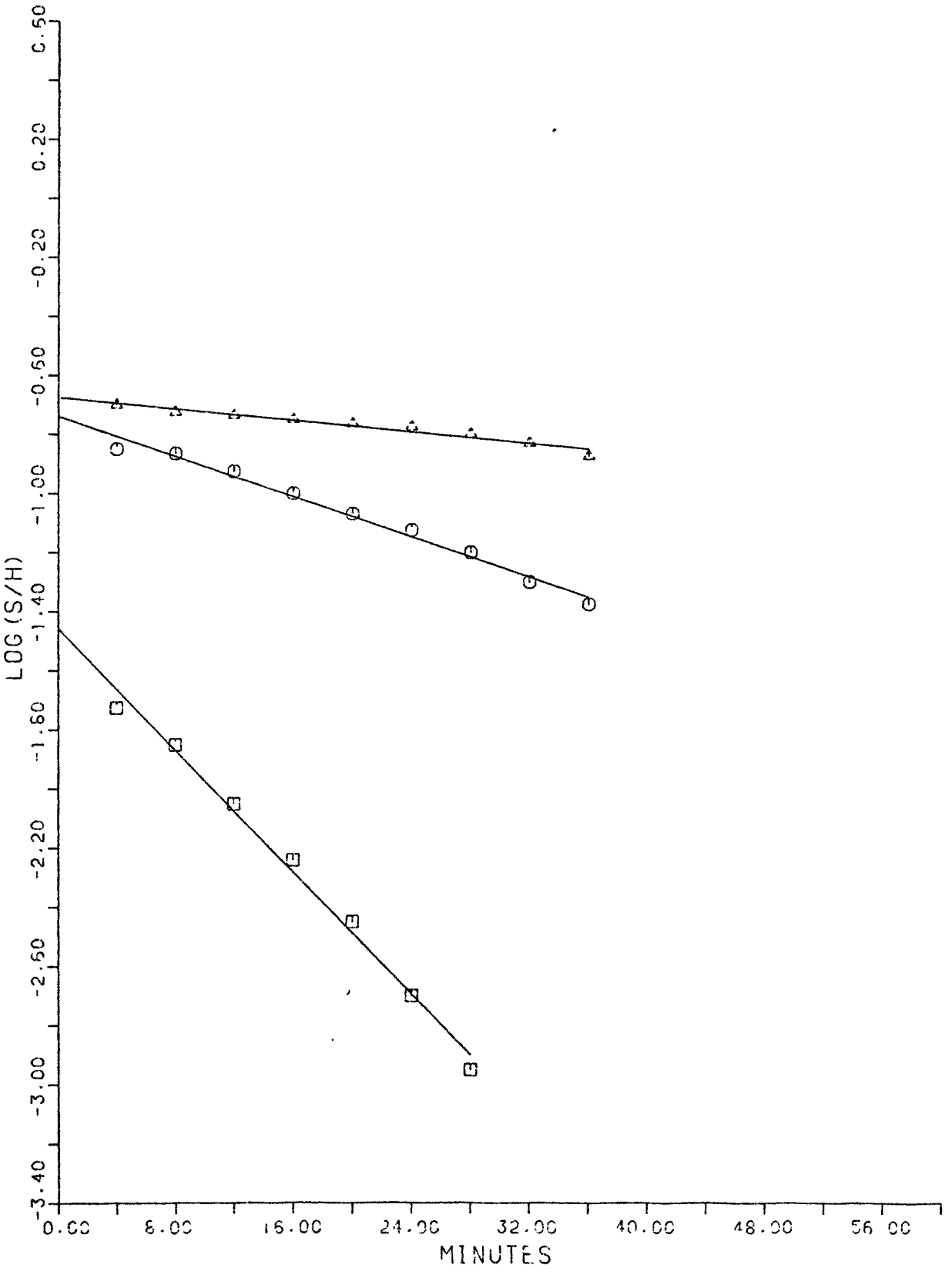

Fig. 9. Second order rate plots for the reaction of t-BuO_2H with phenyl methyl sulfide at 30°C in $CDCl_3$ and $CHCl_3$ in the presence of $Mo(CO)_6$. Δ = NMR #1, o = NMR #2. □ = titrations.

Reactions in absolute ethanol

Unlike the diphenyl sulfide case, the UV spectra of $PhSCH_3$, $PhSOCH_3$ and $PhSO_2CH_3$ are so similar as to rule out this method of analysis. Therefore reactions were followed by iodometric titrations alone.

For the uncatalyzed reaction, a 1:1 stoichiometry, uncomplicated by oxidation to the sulfone could be assumed. At 65°C the second-order rate constant, k_2, ($-\partial[RO_2H]/\partial t = k_2[RO_2H][PhSCH_3]$), was found to be 3.48×10^{-5} M^{-1} s^{-1}, (Figure 10, Table 11). This is about 10 times larger than the corresponding rate constant for Ph_2S; probably this is an electronic effect, methyl being an electron donor, while, in this instance, phenyl may withdraw electron density.

For reactions catalyzed by $Mo(CO)_6$, it was assumed only that all of the t-BuO_2H consumed was used either to convert sulfide to sulfoxide or sulfoxide to sulfone. Three models were tested for matching computed t-BuO_2H concentrations with experimental values (A, B and C, below). Model C consistently gave good fits to the data, while A and B did not.

A. Rate = $k_3[Mo(CO)_6]_0[ArSMe][t\text{-}BuO_2H] + k_3'[Mo(CO)_6][ArSOMe][t\text{-}BuO_2H]$

B. Rate = $k_3[Mo(CO)_6]_0[t\text{-}BuO_2H][ArSMe]/[1 + K[t\text{-}BuO_2H])$

C. Rate = $k_3[Mo(CO)_6]_0[ArSMe][t\text{-}BuO_2H]$

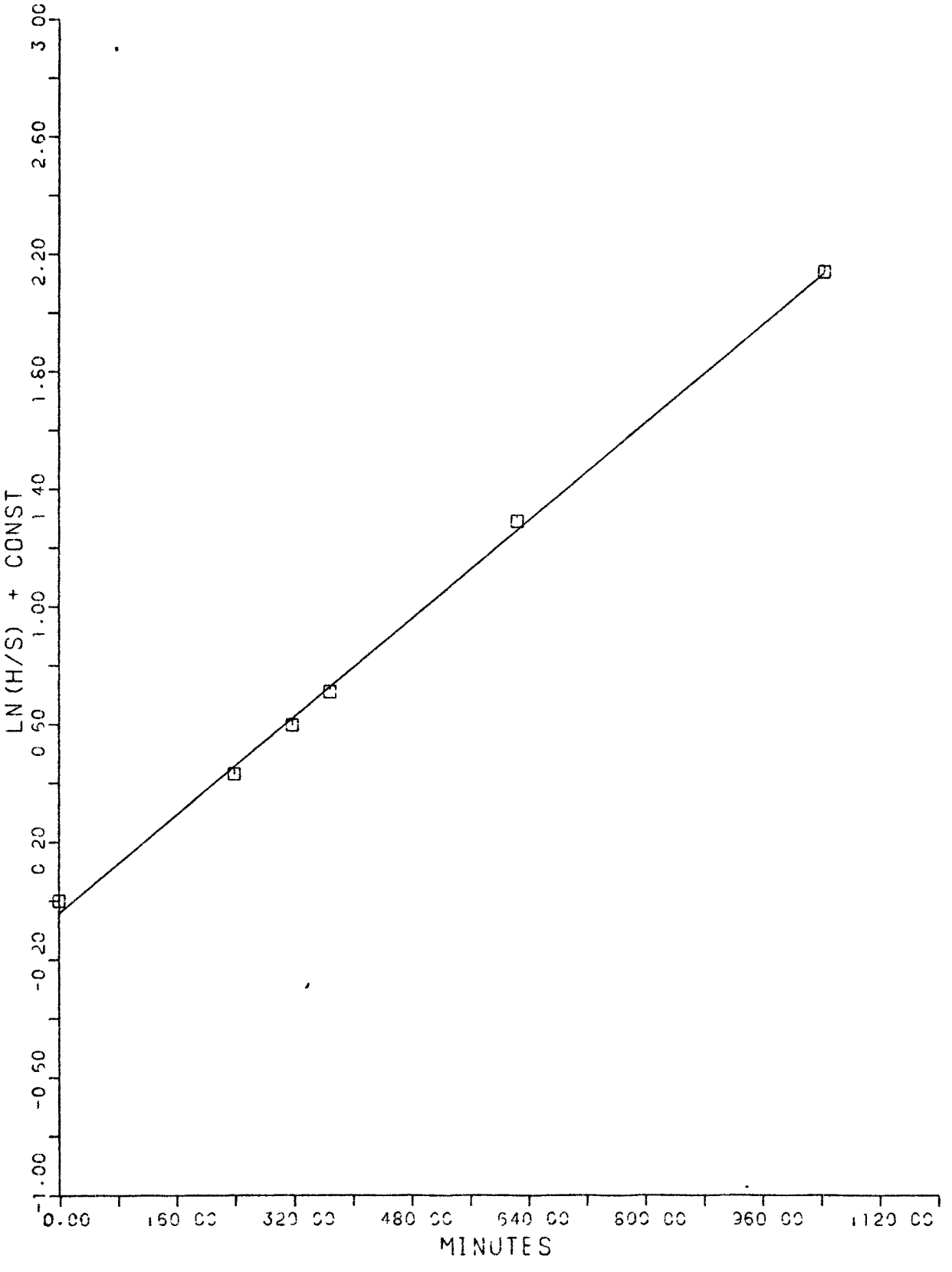

Fig. 10 Second order rate plot for t-BuO_2H oxidation of phenyl methyl sulfide in ethanol at 65°C

TABLE 11

The uncatalyzed oxidation of phenyl methyl sulfide at 65°C in ethanol.

Time (min)	$[t\text{-}BuO_2H]^a$	$[PhSCH_3]^a$	Plot[b]
0	0.7699	0.400	0.0
239	0.664	--	0.4314
317	0.634	--	0.5972
368	0.616	--	0.7102
623	0.546	--	1.2889
1040	0.484	--	2.1363

[a] Mol L^{-1}

[b] $\ell n([R_2S]_0*[RO_2H]/([RO_2H]_0*([RO_2H] - ([RO_2H]_0 - [R_2S]_0)))/([RO_2H]_0 - [R_2S]_0)$

[c] $k = 2.09 \times 10^{-3}\ M^{-1}min^{-1}$; $r = 0.9993$

Results for phenyl methyl sulfide are summarized in Table 12 and for p-chlorophenyl methyl sulfide in Table 13. Figure 11 shows a sample plot.

In only one instance was any significant amount of oxidation to the sulfone observed. This was a run at 65°C with the $Mo(CO)_6$ concentration 100 times that normally used for conveniently measurable rates, and an initial mole ratio of t-BuO_2H to $PhSCH_3$ of 2:1. After 10 minutes, slightly more than 1 equivalent of t-BuO_2H had been consumed, and the concentration of t-BuO_2H continued to decrease with time. Evidently, the sulfoxide to sulfone reaction could be measured, but under conditions where it is difficult to measure the sulfide to sulfoxide conversion.

It was shown that t-BuOH did not inhibit the reaction. Initial addition of t-BuOH in an amount equivalent to initial t-BuO_2H gave no change in the rate (Table 12).

Figure 12 shows an Arrhenius plot of the data from Table 12, giving for molybdenum catalyzed oxidation phenyl methyl sulfide to sulfoxide an E_a of 44.5 kcal and log A = 22.0. These values are very different from those found for Ph_2S, a matter reserved for later discussion.

Another surprising fact is that p-chlorophenyl methyl sulfide reacts somewhat faster than the unsubstituted compound (Table 12 versus Table 13). It is difficult to ascribe significant electron donor character to a para-chlorine. Indeed, in similar reactions, metal-catalyzed oxidations of styrenes (40) and anilines (42), substitution of the ring by chlorine reduces the rate, as expected. This seems to be yet another strange feature of sulfide oxidations.

TABLE 12

$Mo(CO)_6$-Catalyzed reactions of phenyl methyl sulfide with t-BuO_2H in ethanol.[a]

Run #'s[b]	$[t\text{-}BuO_2H]_0$	$[PhSCH_3]_0$	$[Mo(CO)_6]_0 \times 10^3$	T °C	$k(M^{-2}min^{-1})$[c]	Variance
125	0.767	0.400	1.00	25	0.836	0.000066
55, 57[d]	0.413	0.400	2.04	35	17.5	0.0010
60, 54[d]	0.827	0.400	1.03	35	17.0	0.0102
53, 58[d]	0.826	0.400	1.94	35	17.2	0.004
165	0.768	0.423	0.984	45	69.6	0.00249
15	0.100	0.400	0.0101	65	7126.	0.00010
14	0.100	0.400	0.0202	65	6394.	0.00010
09	0.200	0.400	0.0100	65	7885.	0.00010
08	0.200	0.400	0.0201	65	6090.	0.00006
07	0.400	0.400	0.0105	65	9488.	0.0006
06	0.400	0.400	0.0211	65	7697.	0.0010
11	0.800	0.400	0.0101	65	10840.	0.0025
10	0.800	0.400	0.0201	65	7238.	0.0057
16[e]	0.400	0.400	0.0203	65	7618.	0.0010
18, 19	0.400	0.200	0.0102	65	9828.	0.0007
17	0.400	0.200	0.0204	65	8325.	0.0014
23	0.400	0.800	0.0101	65	5427.	0.0077
22	0.400	0.800	0.0202	65	7122	0.0004

[a] In air unless otherwise specified. [b] If more than one run is shown, the results are averaged.

[c] Rate = $k[Mo][RO_2H][PhSCH_3]$; E_a = 44.5 kcal mol^{-1}; log A = 22.0 $M^{-1}s^{-1}$

TABLE 13

$Mo(CO)_6$-catalyzed reactions of p-chlorophenyl methyl sulfide with t-BuO_2H in ethanol.[a]

Run #'s[b]	$[t\text{-}BuO_2H]_0$	$[p\text{-}ClPhSCH_3]_0$	$[Mo(CO)_6]_0 \times 10^3$	T °C	$k(M^{-2}min^{-1})$[c]	Variance
76	0.416	0.422	1.02	35	21.0	0.0008
77,78	0.416	0.422	2.02	35	22.3	0.0009
73,74,75	0.826	0.422	0.989	35	20.6	0.0051
79,80	0.826	0.422	2.01	35	19.6	0.0033

[a] Run in an argon atmosphere

[b] If more than one run is shown, results are averaged.

[c] Rate = $k[Mo][RO_2H][p\text{-}ClPhSCH_3]$

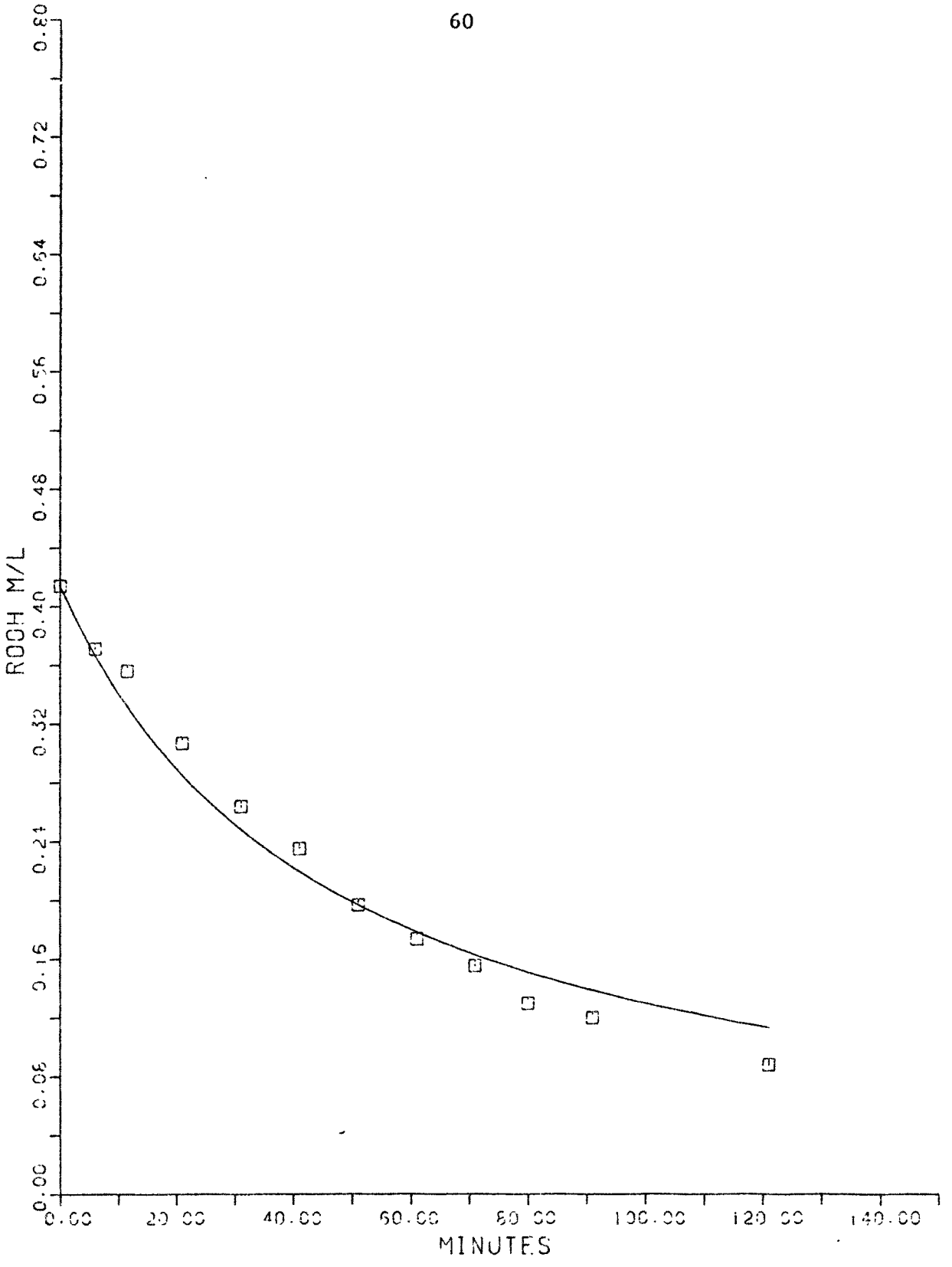

Fig. 11 Concentrations versus time for the oxidation of phenyl methyl sulfide by t-BuO_2H at 35°C in ethanol and in the presence of $Mo(CO)_6$

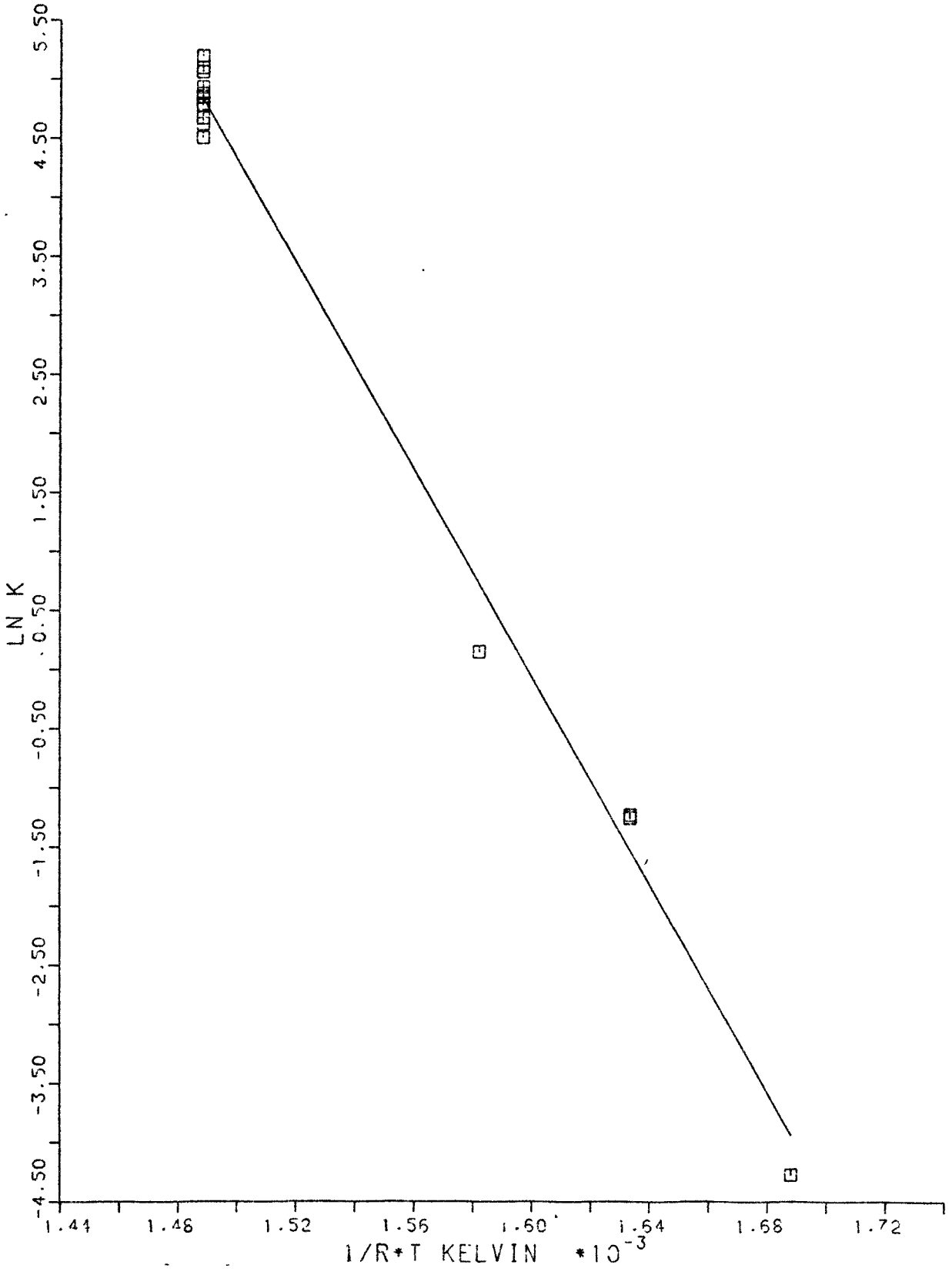

Fig. 12 Arrhenius plot for t-BuO_2H oxidation of phenyl methyl sulfide

Oxidations Using $MoO(O_2)_2 \cdot HMPT$

The molybdenum peroxo complex was prepared by the method of Mimoun et al. (49). It yielded 2 moles of I_2/mol on iodometric titration.

A reaction with diphenyl sulfide (0.2 M Ph_2S, 0.2 M $MoO(O_2)_2 \cdot HMPT$ in ethanol at 35°C), appeared to be complete after 4 hours. The white crystals which precipitated were shown by UV (Appendix 5) and mass spectrometry to be pure diphenyl sulfone.

Reaction with diphenyl sulfoxide (0.2 M Ph_2SO, 0.1 M $MoO(O_2)_2 \cdot HMPT$ in ethanol at 35°C) required 7.5 hours, again yielding the sulfone.

Rate studies were not pursued because iodometric titration of the reaction solutions produced a precipitate, making the end point difficult to observe.

The Mechanism of Metal-catalyzed Oxidation of Organic Sulfides and Sulfoxides by Hydroperoxides

Activation of the catalyst

Both theory and experience suggest that the metal should be in a high oxidation state (see Introduction). For V^{III} or V^{IV} salts or complexes, a small amount of the hydroperoxide is consumed in a rapid spectroscopically observable oxidation to V^{V}. No other species seems to be required for this "activation".

The molybdenum in $Mo(CO)_6$ requires oxidation to Mo^{VI}. Since $Mo(CO)_6$ is a tight, relatively unreactive species, ligand exchange and oxidation might be expected to be less than instantaneous. Short induction periods have been observed both in this work (Figures 4 and

11) and in previous research (41). However, Mo as MoO_3 requires no oxidation, and yet in this work (Figure 2) short induction periods were also found when molybdenum was added in that form.*

In no previous reports has there been any suggestion that the substrate plays a part in the "activation" of a molybdenum catalyst. But in this work, many observations point to the involvement of the organic sulfide, required apparently in much greater than catalytic concentrations. Among these are:

(1) The non-oxidation of diphenyl sulfoxide unless the medium contains, or has previously contained gross concentrations of diphenyl sulfides.

(2) The "best" way to make up a run for sulfide oxidation (EXPERIMENTAL), which was found not to be pre-equilibration of molybdenum species with t-BuO_2H, as might be expected, but rather pre-equilibration of the catalyst with the organic sulfide. The "worst" procedure was no pre-equilibration at all. Such runs showed strong auto-acceleration (Table 14, Figure 14).

(3) Reactions carried out at low (0.1-0.2 M) initial sulfide concentrations gave longer, but unfortunately non-reproducible induction periods. Of two runs carried out at 35°C with initial concentrations of 0.2 M $PhSCH_3$, 0.8 M t-BuO_2H and 0.001 M $Mo(CO)_6$, one gave no reaction for nearly 40 minutes while the other started reacting after 10 minutes.

Finding out just what is going on and what the structural features of the actual catalyst are, requires further work.

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* Solutions of MoO_3 or $Mo(CO)_6$ and t-BuO_2H in ethanol were quite stable, shwoing no loss ot t-BuO_2H for many hours (Figure 13).

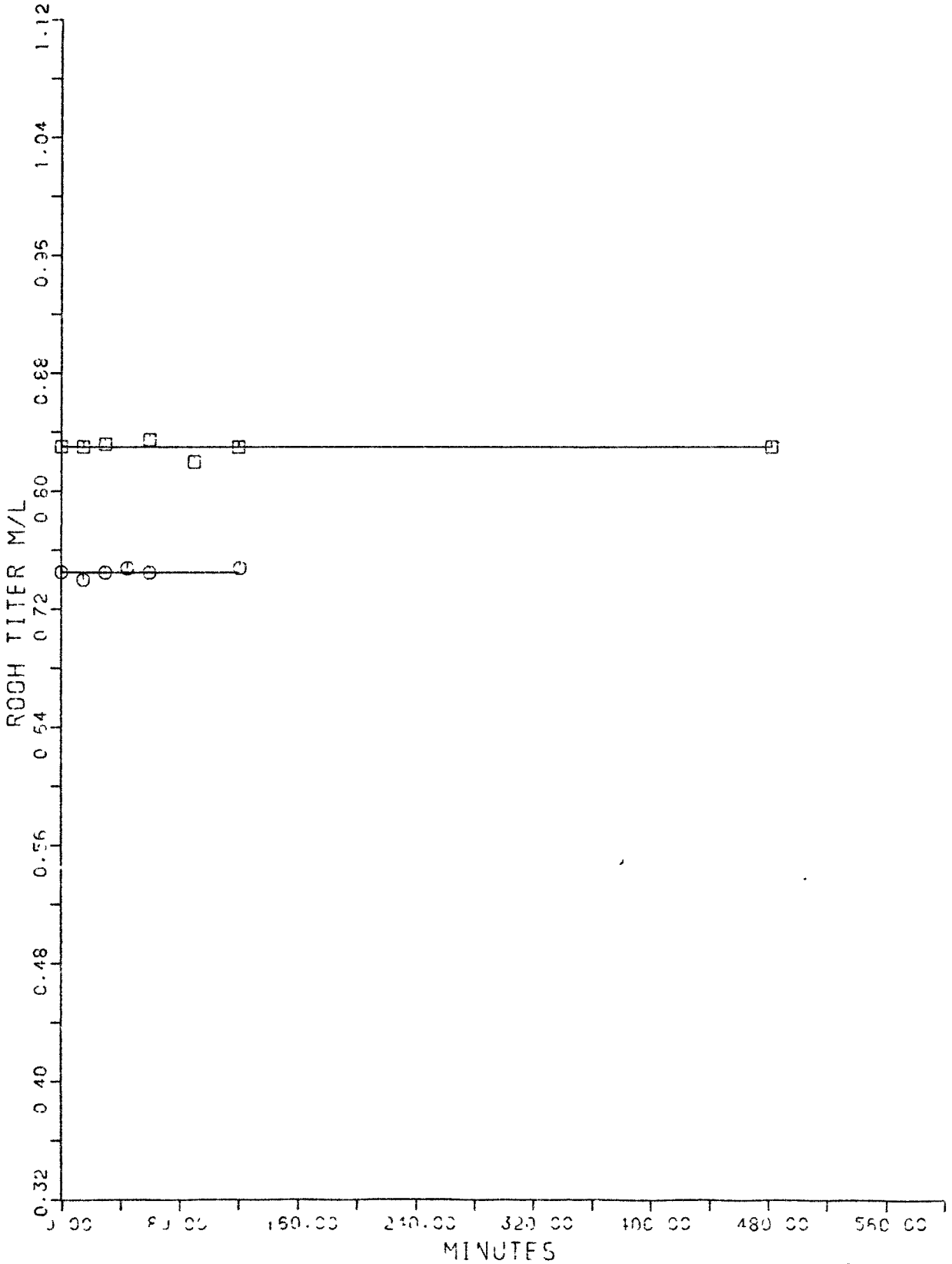


Fig. 13 Concentration of t-BuO_2H versus time in the presence of $Mo(CO)_6$ in ethanol at 35°C and 65°C

TABLE 14

$Mo(CO)_6$-Catalyzed oxidations of phenyl methyl sulfide at 45°C in ethanol showing the effect of different catalyst preparations.[a]

Time (min)	Run #1[b]		Run #2[c]	
	[t-BuO_2H]	[$PhSCH_3$]	[t-BuO_2H]	[$PhSCH_3$]
0	0.713	0.417	0.7678	0.423
10	0.676	--	0.7216	--
20	0.653	--	0.6176	--
30	0.619	--	0.5248	--
40	0.590	--	0.4461	--
50	0.555	--	0.3986	--
60	0.532	--	0.3733	--
70	0.505	--		
80	0.476	--		
90	0.449	--		
100	0.424	--		

[a] Under argon with $Mo(CO)_6 = 1.0 \times 10^{-3}$ M

[b] Catalyst added as solution in ethanol at the start of the reaction.

[c] Catalyst and $PhSCH_3$ dissolved together in ethanol and kept at 45° for one hour before adding t-BuO_2H to start the reaction.

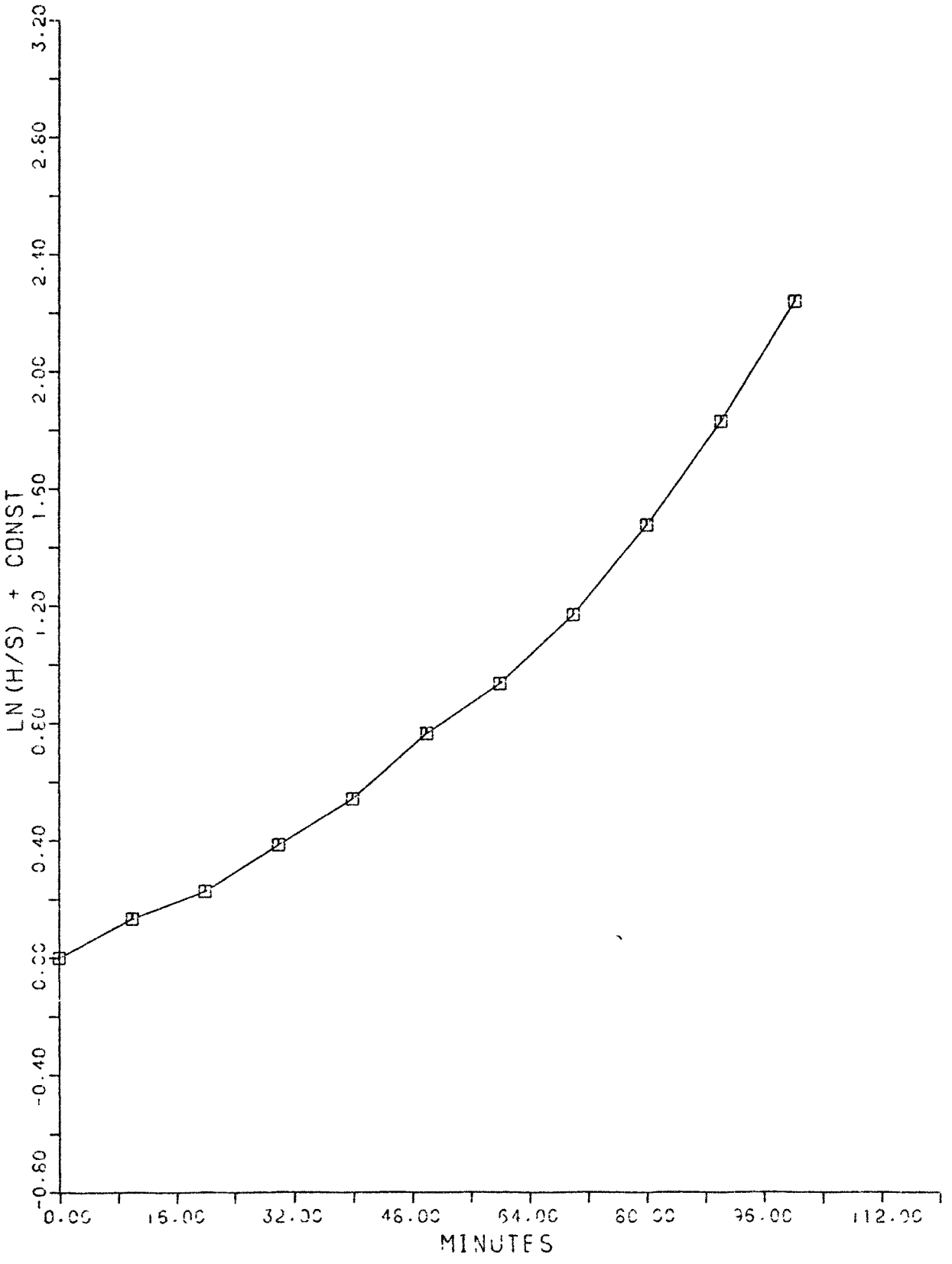


Fig. 14 Second-order rate plot for the $Mo(CO)_6$-catalyzed oxidation of phenyl methyl sulfide by t-BuO_2H where the sulfide and catalyst were not pre-equilibrated

Complexation of the metal ion

Two types of evidence have, in the past, suggested that it is the metal ion-hydroperoxide complex that leads to reaction rather than a metal ion-oxidizable substrate complex (INTRODUCTION).

(1) Substituents which increase electron density at the reactive site of the substrate facilitate reaction, showing that the function of the substrate is nucleophilic. The substrate may very well form complexes with the metal ion, but the effect would be to make them less nucleophilic. Moreover, the hydroperoxide bond required a decrease in electron density in order to make it receptive to nucleophilic attack; this presumably is the purpose of the metal ion.

(2) High concentrations of hydroperoxide, but not of substrate, frequently lead to saturation effects similar to enzyme-substrate reactions. That is, if more than a small fraction of the metal ions are complexed by a reactant to form a reactive intermediate, the concentration of the intermediate does not increase linearly with increased concentration of the reactant.

The fact that molybdenum-catalyzed reactions usually do not show saturation effects indicates that Mo^{VI} complexes the hydroperoxide weakly.

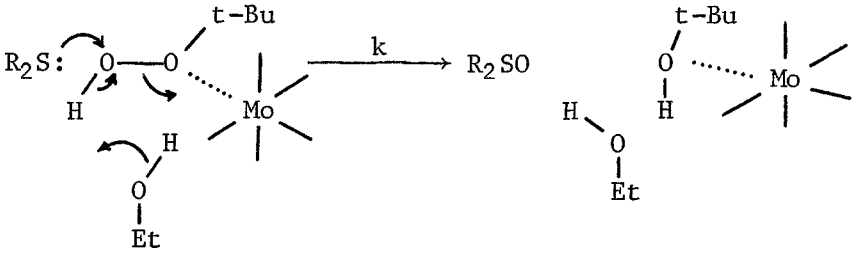
$$t\text{-}BuO_2H + Mo^{VI}L_6 \overset{K}{\rightleftharpoons} t\text{-}Bu\text{-}\underset{\underset{H}{|}}{\underset{|}{O}}\text{---}Mo^{VI}L_5 + L \qquad [35]$$

where L represents any ligand.

As explained by Kochi (34) (INTRODUCTION), competition by the alcohol formed by reduction of the hydroperoxide for the metal ion may lead to a rate expression identical to that for saturation. With ethanol as the solvent, however, this could hardly be a factor, since the concentration of total alcohol remains effectively constant throughout the reaction.

Reaction of the substrate with the complex

The mechanism shown in Equation (36) has been proposed by Modena et al. (46).



[36]

It is essentially the same as has been proposed for other substrates (36, 37), and would apply equally well to sulfoxides.

The rate expressions follow:

$$-\partial[R_2S]/\partial t = k(complex][R_2S] \quad [37]$$

$$-\partial[R_2S]/\partial t = kK[RO_2H][MoL_6][R_2S] \quad [38]$$

$$\partial[R_2SO_2]/\partial t = k'K[RO_2H][MoL_6][R_2SO] \quad [39]$$

(where k' is the rate constant analogous to k for R_2SO as substrate)

$$\partial[R_2SO]/\partial t = -\partial[R_2S]/\partial t - \partial[R_2SO_2]/\partial t \quad [40]$$

$$-\partial[t\text{-}BuO_2H]/\partial t = -\partial[R_2S]/\partial t - \partial[R_2SO_2]/\partial t \quad [41]$$

(since an insignificant amount of t-BuO_2H is complexes at any given time)

In the case that $k >> k'$ and $[R_2S] > [R_2SO]$,

$$-\partial[t\text{-}BuO_2H]/\partial t = kK[RO_2H][MoL_6][R_2S] \quad [42]$$

This work has shown equation 42 to apply to the oxidations of diphenyl sulfide and phenyl methyl sulfide in ethanol using $Mo(CO)_6$. The first-order dependence on $[RO_2H]$ was demonstrated over an eightfold range in initial t-BuO_2H concentrations. In fact, the first order dependence on $[R_2S]$ and on $[RO_2H]$ is established for catalysis by MoO_3 in ethanol and for $Mo(CO)_6$ in $CDCl_3/CHCl_3$ as well.

This contrasts with the results of Modena _et al._ (46) for n-Bu_2S, t-BuO_2H and $MoO_2(acac)_2$ in ethanol. The rate expression is

$$-\partial[RO_2H]/\partial t = k[MoL_6][R_2S][t\text{-}BuO_2H]/(1 + K[t\text{-}BuO_2H]) \quad [43]$$

(where k and K are not related to equations 35-42)

Equation 43 (developed in Appendix 7) implies saturation of the catalyst by t-BuO_2H; _i.e._, a relatively strongly bonded molybdenum-hydroperoxide complex. The only real difference between Modena's work and that reported here is the sulfide. (The particular molybdenum compound thrown into the pot has little or no effect on the reaction subsequent to formation of active catalyst (36, 37).)

The enormous effect even a small change in sulfide structure can have is shown by the apparent activation energies, 18.5 kcal for Ph_2S and 44.5 kcal for $PhSCH_3$. From equation 42, these are really thermal coefficients for kK, or the sums of E_a for reaction 36 and E for equilibrium 35. It cannot be seriously argued that replacing a phenyl by methyl would increase the activation energy for nucleophilic substitution (reaction 36) by nearly 30 kcal. Ordinarily it would seem equally unlikely that an equilibrium should be so affected.

CONCLUSION

The results of this work fall short of the objectives stated in the introduction, but are more interesting. An apparently straight forward reaction has proved to be not simple at all.

The most striking discovery, perhaps, is the oscillating reaction. Clearly oxygen is required, and thus it is easy to avoid. Unfortunately the other requirements for getting it started are not so easy to determine. The real cause may have been a trace impurity in one of the reactants.

The non-reactivity of diphenyl sulfoxide unless the catalyst has been liberally doped with the sulfide is also puzzling. If a high concentration of sulfide is necessary, why does the reaction keep going when the sulfide is apparently all gone? IF the active catalyst is active because of some tightly bound sulfide ligands, why was a large amount of sulfide necessary in the first place?

Finally, the differences in behaviour of diphenyl sulfide, phenyl methyl sulfide and di-n-butyl sulfide are so great as to be hard to believe. But the data appear to be reliable. One is forced to conclude that the sulfide has a profound influence on the structure of the active catalyst. What that structure is remains to be seen.

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APPENDICES

APPENDIX 1

```
R CSEFA/TABLE1

#RUNNING 0037
 TABLE (1):THREE SETS OF RESULTS WHICH ARE OBTAINED FROM TWO
           DIFFERENT METHODS.
```

TIME MIN.	H NMR#1 T-BUO2H	H NMR#2 T-BUO2H	TITRATIONS#1 T-BUO2H
0	2.010	2.094	2.050
4	1.993	1.979	1.785
8	1.958	1.879	1.748
12	1.952	1.776	1.702
16	1.927	1.679	1.621
20	1.904	1.593	1.559
24	1.874	1.508	1.501
28	1.830	1.445	1.463
32	1.780	1.384	1.402
36	1.733	1.322	1.359
40	1.646	1.274	1.319
52	1.329	1.171	1.232

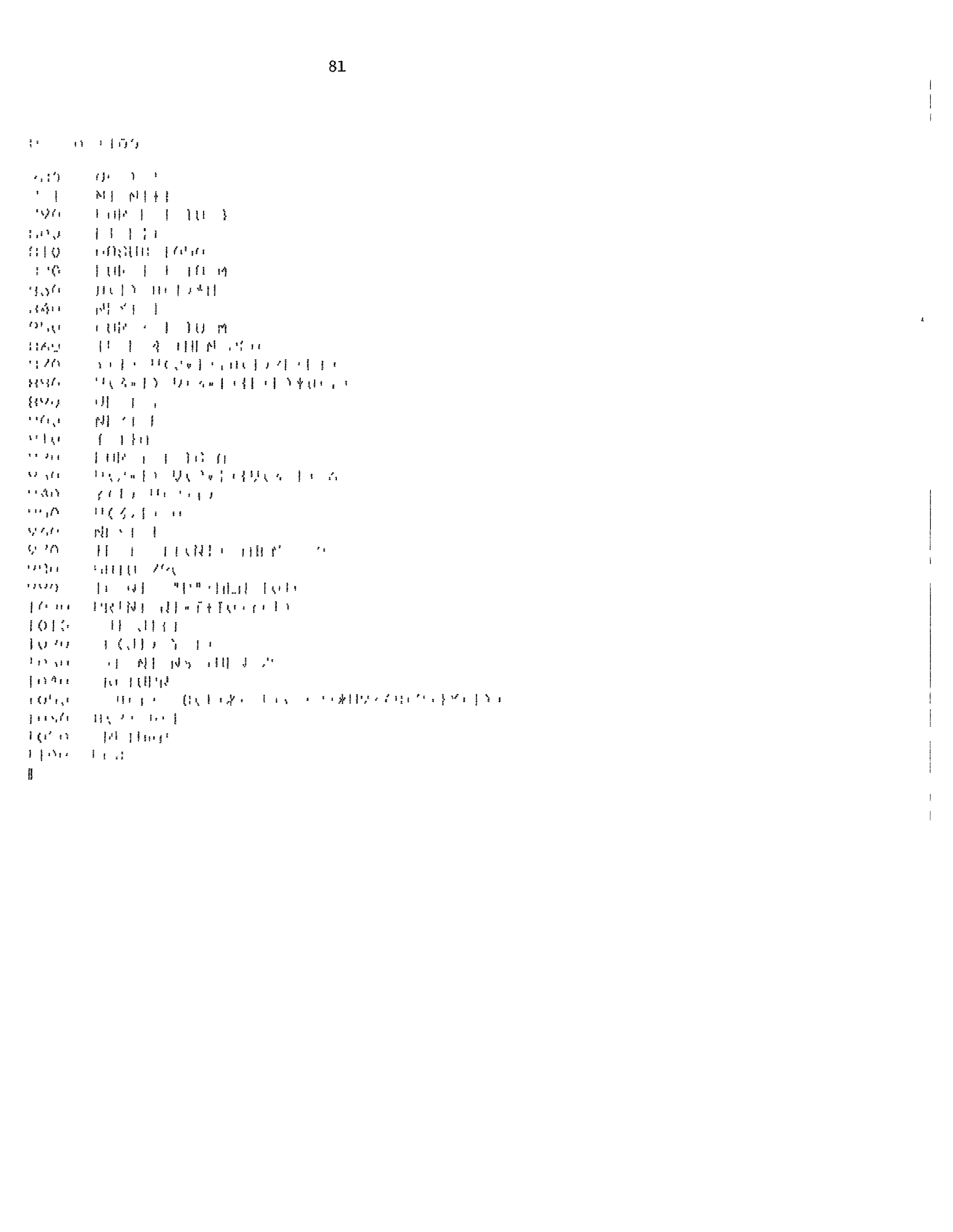
```
 H NMR#1,2  AT 30C AND IN CDCL
 TITRATIONS#1    AT 30C AND IN CHCL
#ET=39.5 PT=0.3 IO=1.1
```

APPENDIX 2

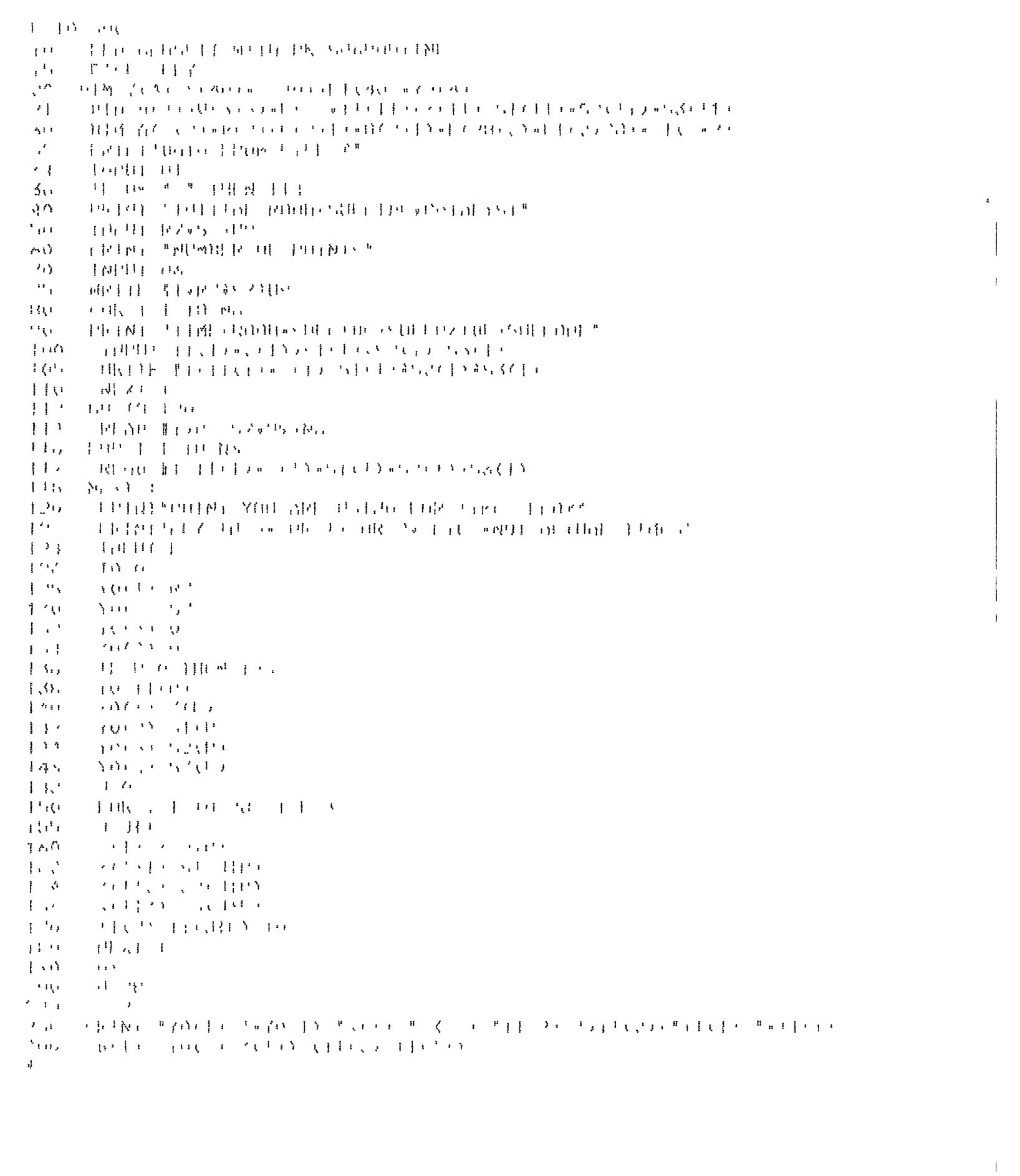
```
```

```
```

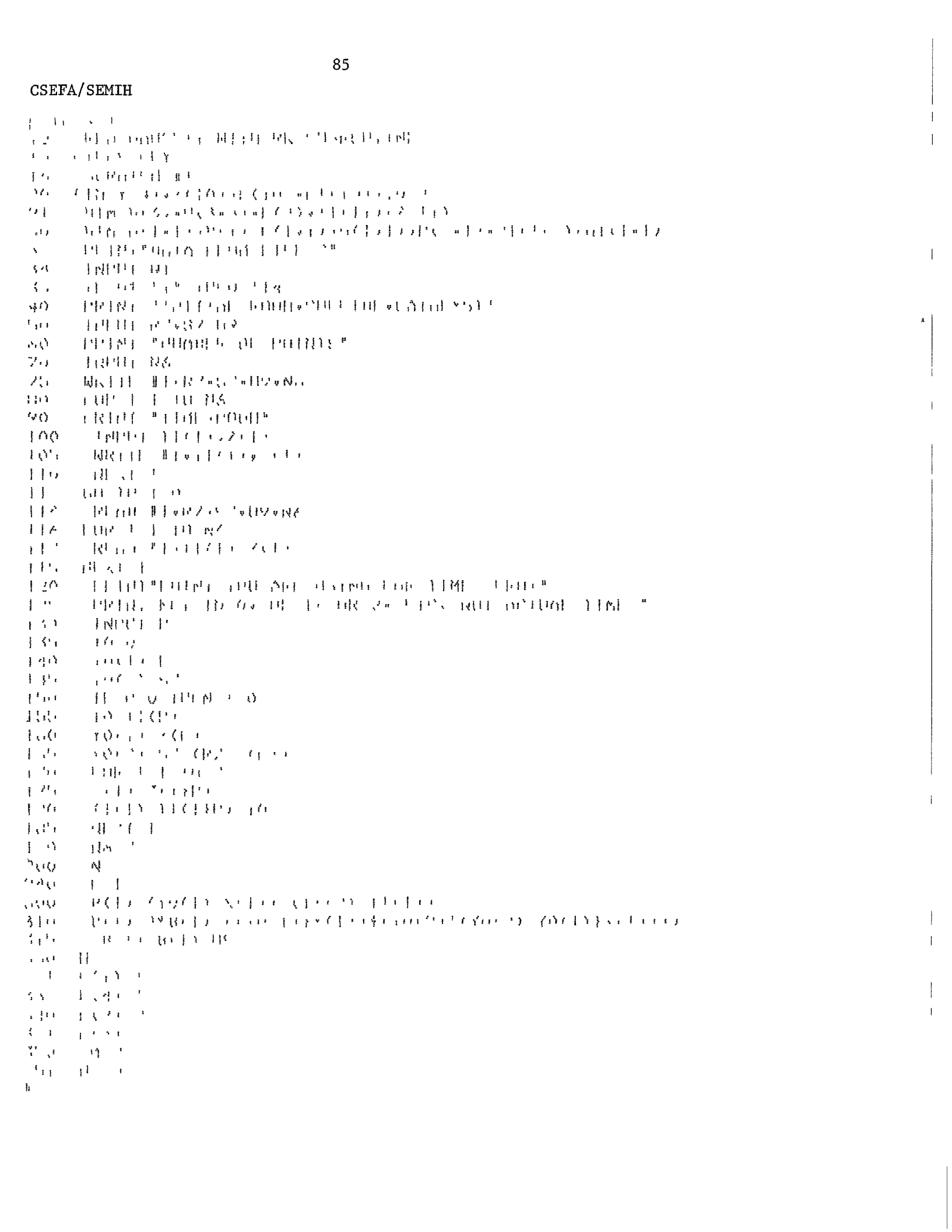
CSEFA/SEFA

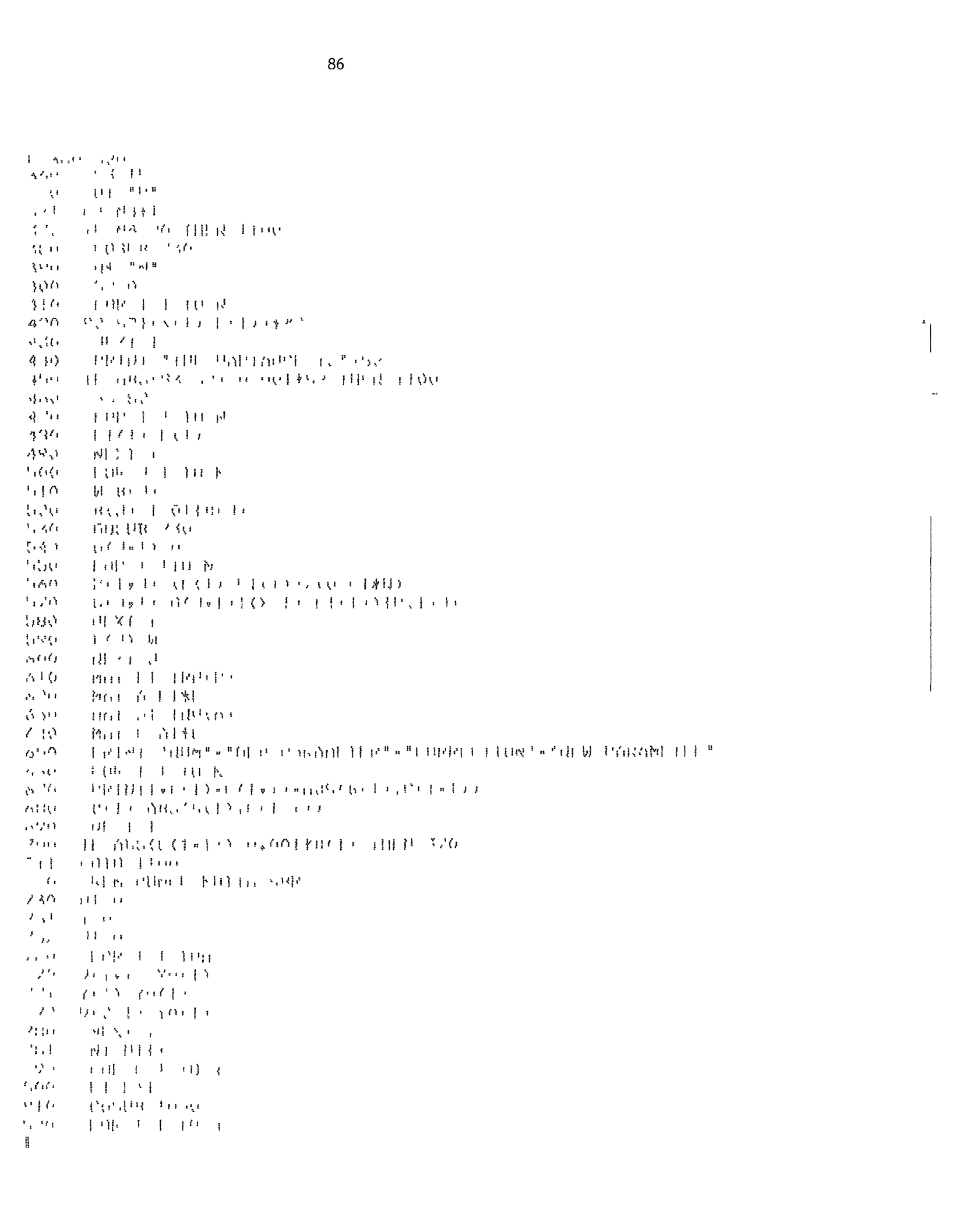


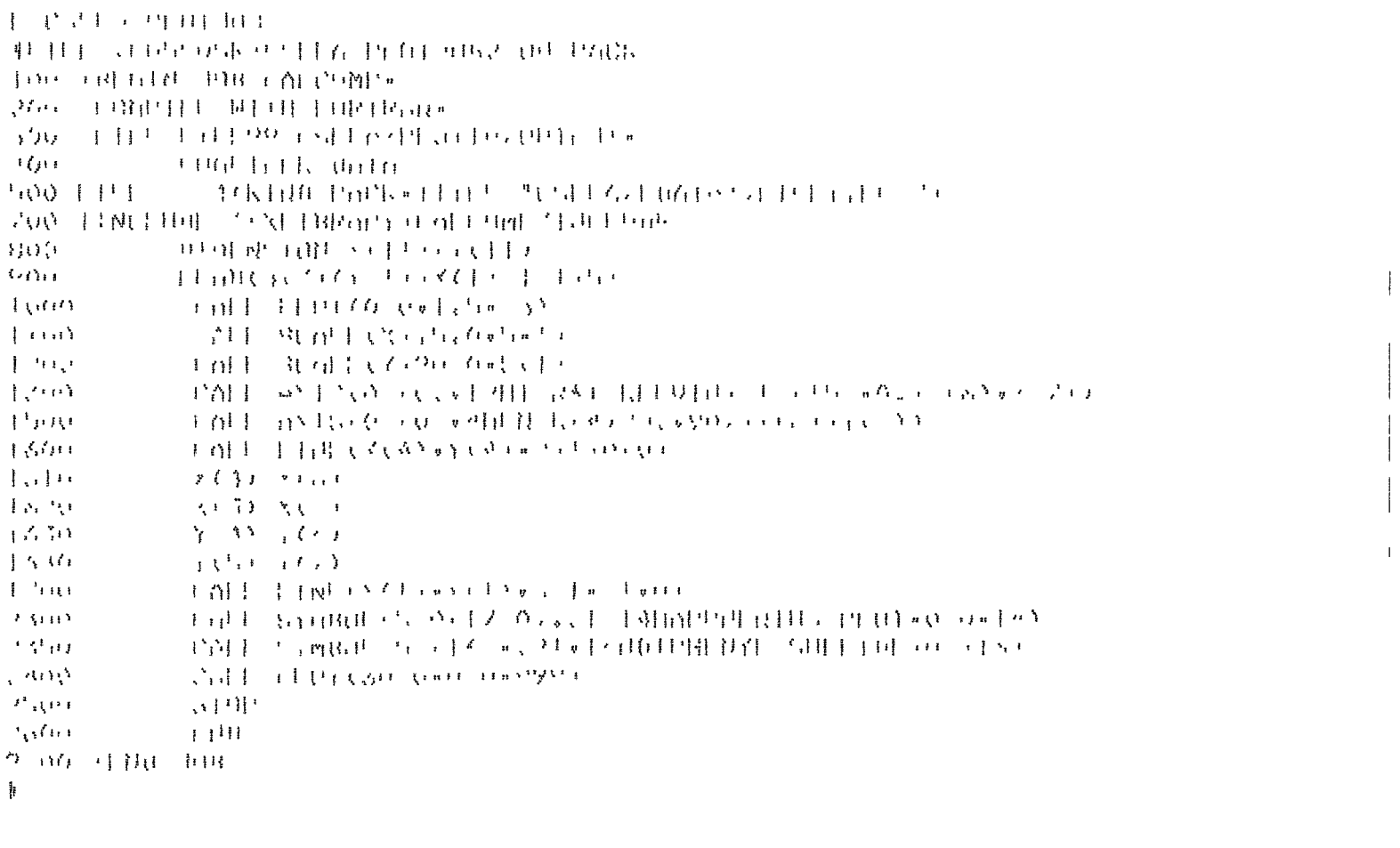
CSEFA/SEMIH2

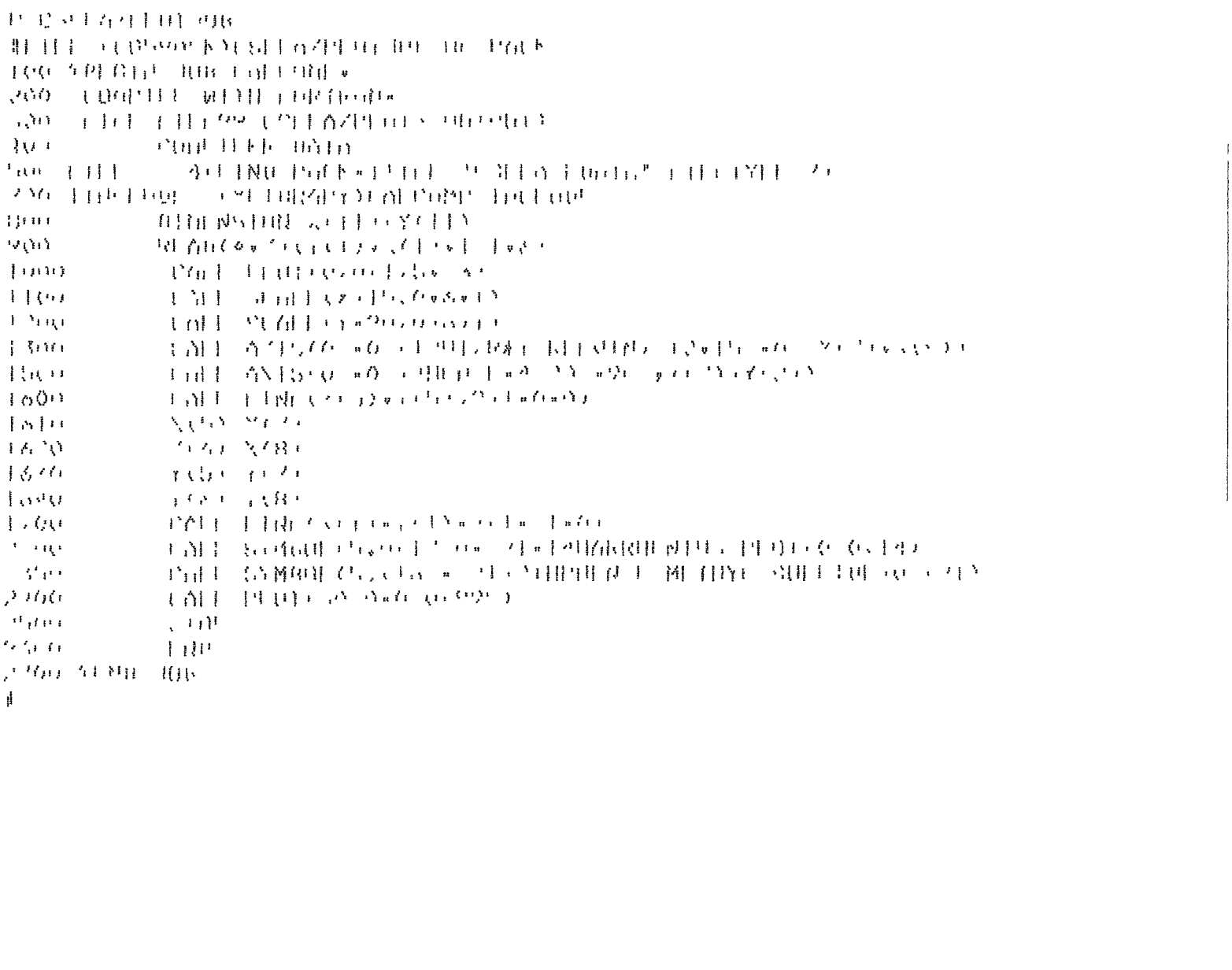


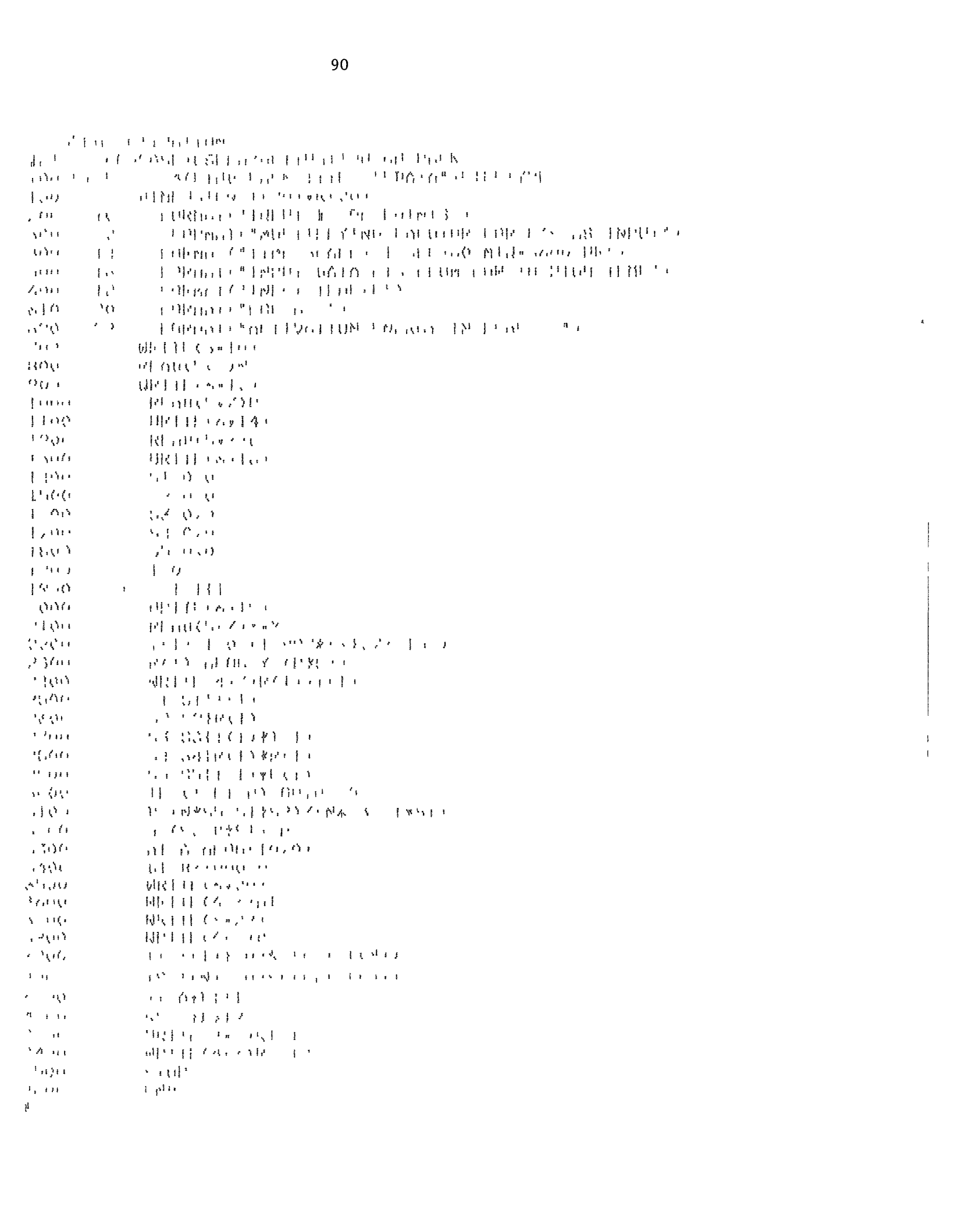
CSEFA/SEMIH











Program for recording

```
5 PRINT "PROG1 ON SULFIDE OXIDN DATA TAPE 'SEFA DATA 1'"
10 DIM L1(12),T(15),O(15,12),T1(15),R1(15),Q$1
20 DATA LOAD "FREC":DATA LOAD F:BACKSPACE 1F
30 INPUT "DATE OF RUN,RUN NUMBER, NOTEBOOK PAGE,TEMP,SOLVENT,INIT PEROXIDE CON
C,INIT SULFIDE CONC.,MOLYB CONC,DILUTION FACTOR FOR UV,NO OF UV PTS",D$,RO,NO,
T5,S$,HO,SO,MO,D6,U6
35 INPUT "NO OF UV LAMBDA'S USED,NO OF TITRATION PTS",L,T6
40 PRINT "KEY IN LAMBDA VALUES STARTING WITH LOWEST":FOR I= 1 TO L:INPUT "LAMB
DA",L1(I):NEXT I
50 PRINT "KEY IN TIME (MIN) FOR O.D. READINGS, FOLLOWED BY O.D.'S": FOR I= 1 T
O U6:INPUT "TIME",T(I):FOR J= 1 TO L:PRINT L1(J);" NM: O.D. = ";:INPUT O(I,J):
PRINT :NEXT J:NEXT I
60 PRINT "KEY IN TIMES AND TITRATION VALUES FOR PEROXIDE CONC":FOR I=1 TO T6:I
NPUT "TIME, PER CONC",T1(I),R1(I):NEXT I
70 PRINT "THE INPUT WILL NOW BE LISTED FOR ERROR CHECK. TURN ON TYPEWRITER,PLE
ASE":STOP
75 SELECT PRINT 211
80 PRINT "DATE OF RUN(D$) ";D$;"  RUN NO(RO) ";RO;"  NOTEBOOK PAGE(NO) ";NO:PR
INT
90 PRINT "TEMP(T5) ";T5;"  SOLVENT(S$) ";S$;"  DILUTION FACTOR(D6) ";D6:PRINT

100 PRINT "INIIT CONC'S: PEROXIDE(HO) ";HO;"  SULFIDE(SO) ";SO;" MOLYB(MO) ";M
O:PRINT
```

```
110 PRINT "NO OF UV PTS(U6) ";U6;" NO OF LAMBDA'S PER PT(L) ";L;"  NO OF TITR
PTS(T6) ";T6:PRINT
120 PRINT "LAMBDA'S","TIMES AND O.D.'S":PRINT :PRINT "    ";:FOR I = 1 TO U6:
PRINTUSING 200,T(I);:NEXT I:PRINT
130 FOR I= 1 TO L:PRINT L1(I);" ";:FOR J= 1 TO U6:PRINTUSING 210,O(J,I);:NEXT
J:PRINT :NEXT I
140 PRINT :PRINT "TIMES AND TITRATION VALUES"
150 FOR I = 1 TO T6:PRINTUSING 200,T1(I);:NEXT I:PRINT :FOR I=1 TO T6:PRINTUSI
NG 210,R1(I);:NEXT I:PRINT
160 SELECT PRINT 005:PRINT HEX(03):PRINT :PRINT
170 PRINT "YOU CAN DO CORRECTIONS IN ACTIVE MODE AT NEXT STOP. SIMPLY KEY IN [
SYMBOL] = [CORRECT VALUE].  MOST SYMBOLS HAVE BEEN GIVEN IN THE PRINT OUT."
175 PRINT "FOR THE REST: LAMBDA'S ARE L1(I), UV TIMES ARE T(I),O.D. VALUES ARE
 O(I,J), TITR TIMES ARE T1(I), TITR VALUES ARE R1(I)":STOP :INPUT "RE-PRINT, Y
ES OR NO",Q$:IF Q$="Y" THEN 75
180 PRINT "IS ALL CORRECT? THE NEXT 'CONTINUE' MAKES THE TAPE !":STOP :GOTO 30
0
200%####.#
210%##.###
300 F=F+1:DATA LOAD "FREC":DATA RESAVE F:SKIP FF
310 DATA SAVE OPEN "DFILE":DATA SAVE D$,R0,N0,T5,S$,H0,S0,M0,D6,U6,L,T6,L1(),T
(),O(),T1(),R1():DATA SAVE END :REWIND
999 END
```

Program for UV data

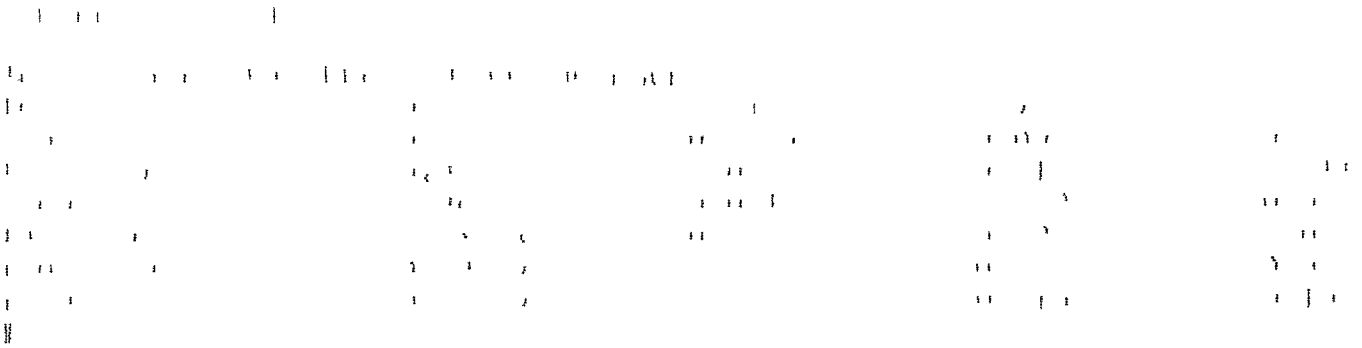
```
 5 PRINT "PROG3 ON SEFA 1,A READER AND CALCULATOR FOR SEFA DATA 1"
8 COM T(15),Z(15,4),U6
10 DIM L1(12),O(15,12),T1(15),R1(15),A(5,1),B(5,5),C(5),D(5,5),E(10),V(10),W(1
0),R(10,3),G(10),Q$1
15 INPUT "DATE OF THIS CALCULATION",Z$:INPUT "ONLY FINAL RESULTS",Q$
20 INPUT "RUN NO",R9
22 DATA LOAD "DFILE":DATA LOAD D$,R0,N0,T5,S$,H0,S0,M0,D6,U6,L,T6,L1(),T(),O()
,T1(),R1():IF R0[]R9 THEN 22
25 INPUT "NO OF VARIABLES",N:MAT REDIM B(N,N),A(N,1):U=0
30 DATA 1,2.1552,2.3013,1,2.3988,2.9715,1,1.4688,1.9875,1,.60727,.82374,1,.310
66,.24662,1,.29358,.20637,1,.36481,.34185,1,.37275,.4326,1,.29634,.28161,1,.21
672,.27304
35 FOR I=1 TO L:FOR J=1 TO N:READ R(I,J):NEXT J:NEXT I
40 U=U+1:FOR I=1 TO L:V(I)=O(U,I):NEXT I:P=1:SELECT PRINT 211
45 FOR I=1 TO L:G(I)=O(1,I)*D6/S0:NEXT I
50 MAT A=ZER:MAT B=ZER:FOR K=1 TO L:FOR I=1 TO N:E(I)=R(K,I)*G(K):NEXT I
60 FOR J=1 TO N:FOR I=1 TO N:B(J,I)=B(J,I)+E(J)*E(I):NEXT I
70 A(J,1)=A(J,1)+E(J)*V(K):NEXT J:NEXT K
90 MAT D=INV(B):MAT C=D*A
100 S=0
110 FOR I= 1 TO L:W(I)=0
120 FOR J=1 TO N:E(J)=R(I,J)*G(I):W(I)=W(I)+C(J)*E(J):NEXT J:S=S+(V(I)-W(I))!2
:NEXT I
125 FOR I=1 TO N:C(I)=C(I)*D6:NEXT I
```

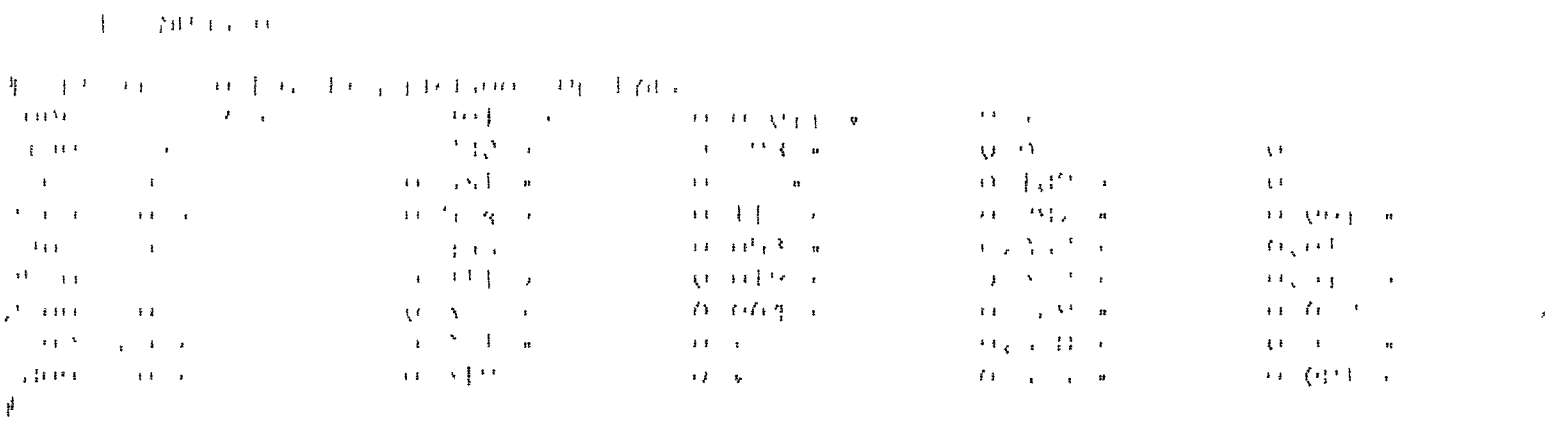
```
130 IF Q$="Y"THEN 150:IF P]1 THEN 140:PRINT "WORKING DATA":PRINT "VARIANCE","S
ULFIDE","SULFOXIDE","SULFONE":PRINT
140 PRINT S,C(1),C(2),C(3)
150 S1=0:FOR I=1 TO N:C(I)=ABS(C(I)):S1=S1+C(I):NEXT I
160 IF S1]1.01*S0 THEN 200:IF S1[.99*S0 THEN 200
170 FOR I=1 TO 3:Z(U,I+1)=C(I):NEXT I:Z(U,1)=R1(U):IF Q$="Y"THEN 190:PRINT :PR
INT "LAST DATA SET SERVES FOR TIME ";T(U);" MIN":PRINT :PRINT "LAMBDA'S","SULF
IDE EPSILONS"," O.D.'S","SUM C(I)E(I)":PRINT
180 FOR I=1 TO L:PRINT L1(I),G(I),V(I),W(I):NEXT I:PRINT :PRINT
190 IF U=U6 THEN 350:GOTO 40
200 P=P+1:IF P]3 THEN 170:FOR I=1 TO L:G(I)=G(I)*S1/S0:NEXT I:GOTO 50
350 PRINT "DATE OF CALCULATION = ";Z$:PRINT
360 PRINT TAB(20),"SUMMARY":PRINT :PRINTUSING 540,"PT","MIN","ROOH","SULFIDE",
"SULFOXIDE","SULFONE"
370 FOR I=1 TO U6:PRINTUSING 550,I,T(I),Z(I,1),Z(I,2),Z(I,3),Z(I,4):NEXT I:PRI
NT :PRINT :IF Q$="Y"THEN 500
400 PRINT "DATE OF RUN(D$) ";D$;"  RUN NO(R0) ";R0;"  NOTEBOOK PAGE(N0) ";N0:P
RINT
430 PRINT "TEMP(T5) ";T5;"  SOLVENT(S$) ";S$;"  DILUTION FACTOR(D6) ";D6:PRINT

440 PRINT "INIT CONC'S: PEROXIDE(H0) ";H0;"  SULFIDE(S0) ";S0;" MOLYB(M0) ";M0
:PRINT
450 PRINT "NO OF UV PTS(U6) ";U6;" NO OF LAMBDA'S PER PT(L) ";L;"  NO OF TITR
PTS(T6) ";T6:PRINT
```

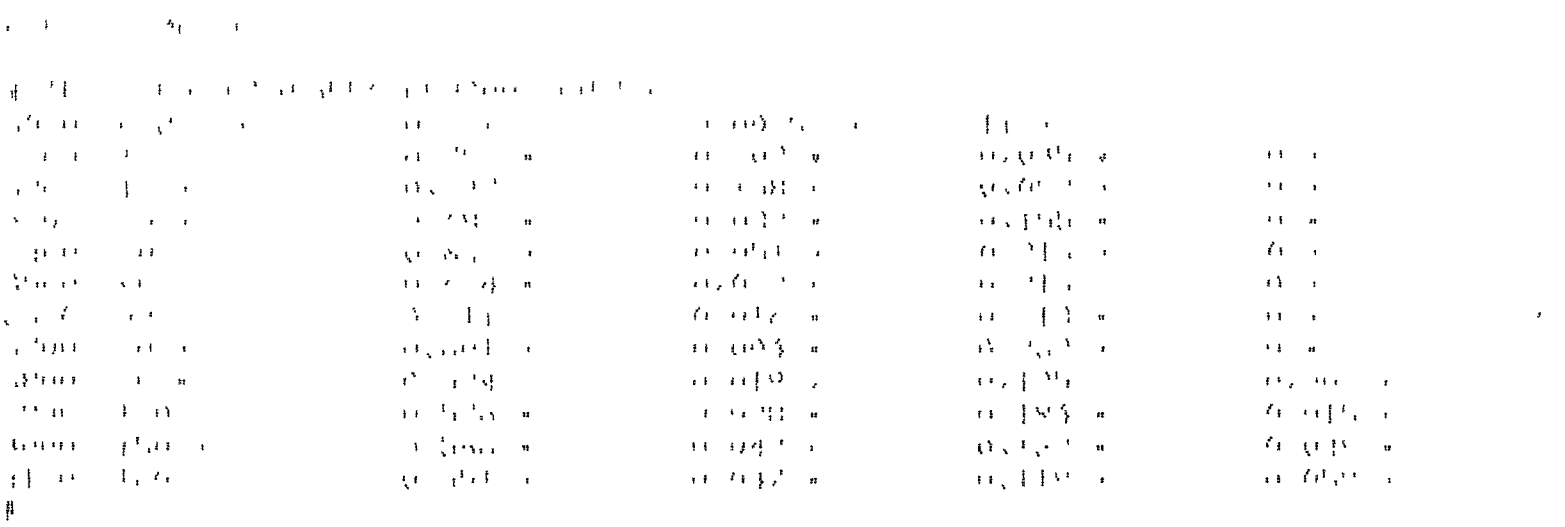
```
460 PRINT "LAMBDA'S","TIMES AND O.D.'S":PRINT :PRINT "    ";:FOR I = 1 TO U6:
PRINTUSING 520,T(I);:NEXT I:PRINT
470 FOR I= 1 TO L:PRINT L1(I);" ";:FOR J= 1 TO U6:PRINTUSING 530,O(J,I);:NEXT
J:PRINT :NEXT I
480 PRINT :PRINT "TIMES AND TITRATION VALUES"
490 FOR I = 1 TO T6:PRINTUSING 520,T1(I);:NEXT I:PRINT :FOR I=1 TO T6:PRINTUSI
NG 530,R1(I);:NEXT I:PRINT
495 Q$="Y":GOTO 350
500 SELECT PRINT 005:INPUT "LOAD GAUSFIT",Q$:IF Q$[]"Y"THEN 510:LOAD "PROG4 "
510 END
520%####.#
530%##.###
540%##     ###        ####       #######      #########    #######
550%##     ###     ##.#####     ##.#####      ##.#####    ##.#####
```

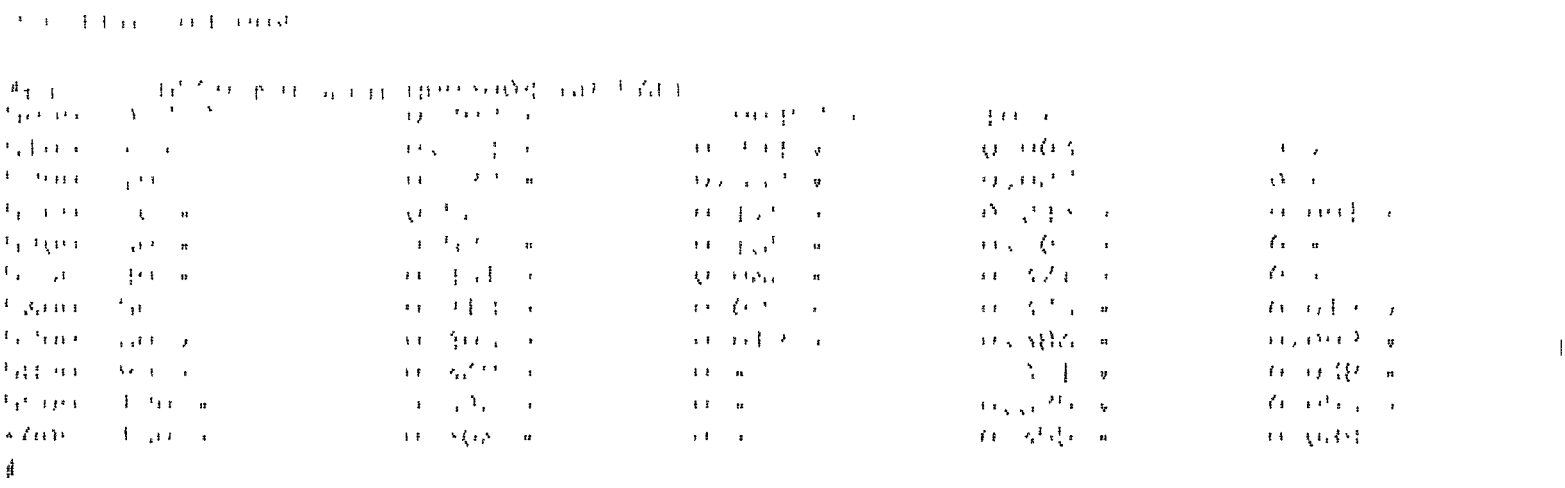
APPENDIX 3

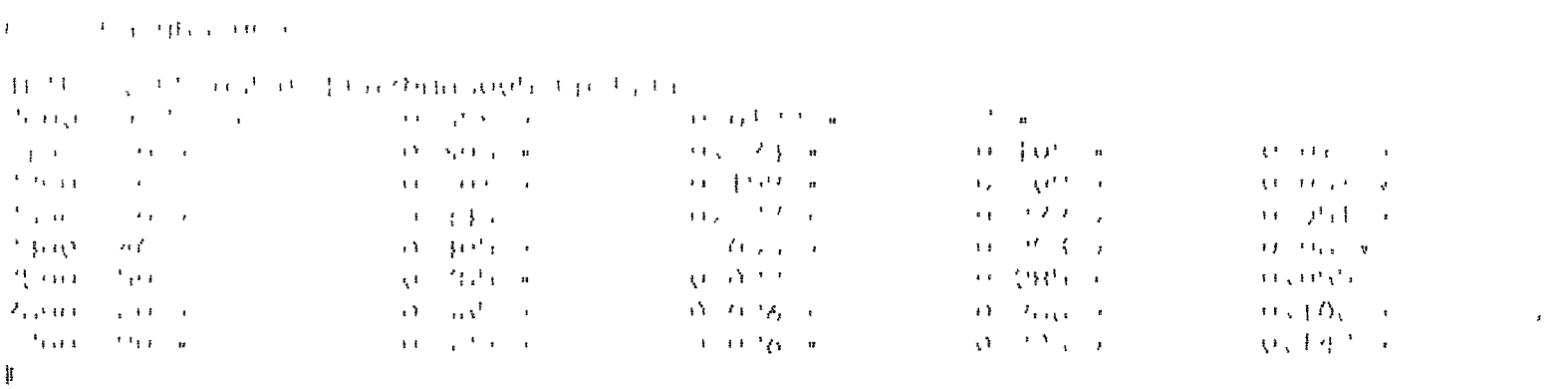
TABLE:9

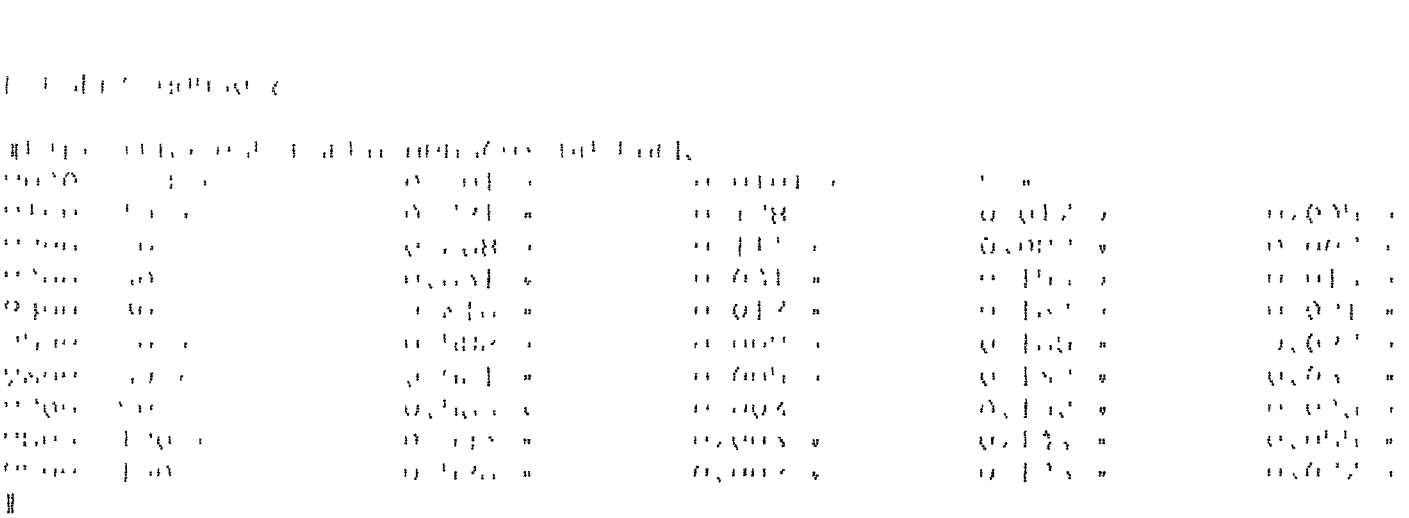




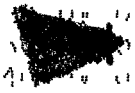


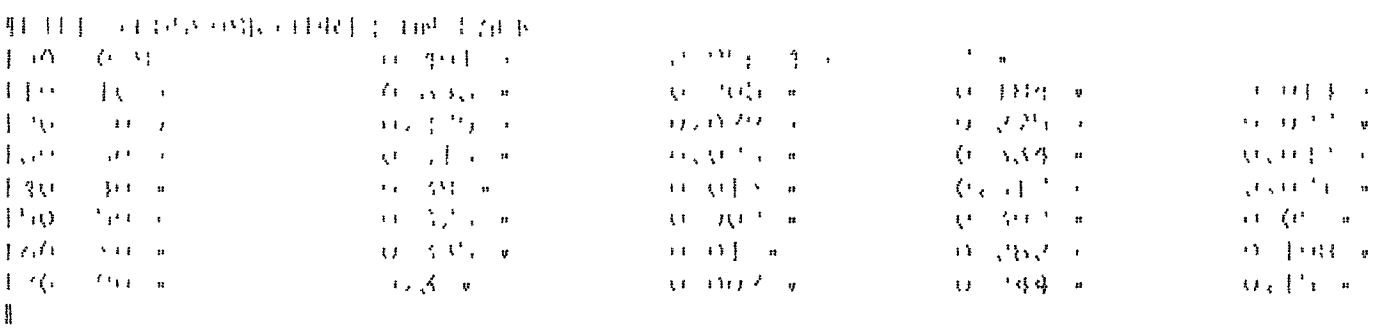


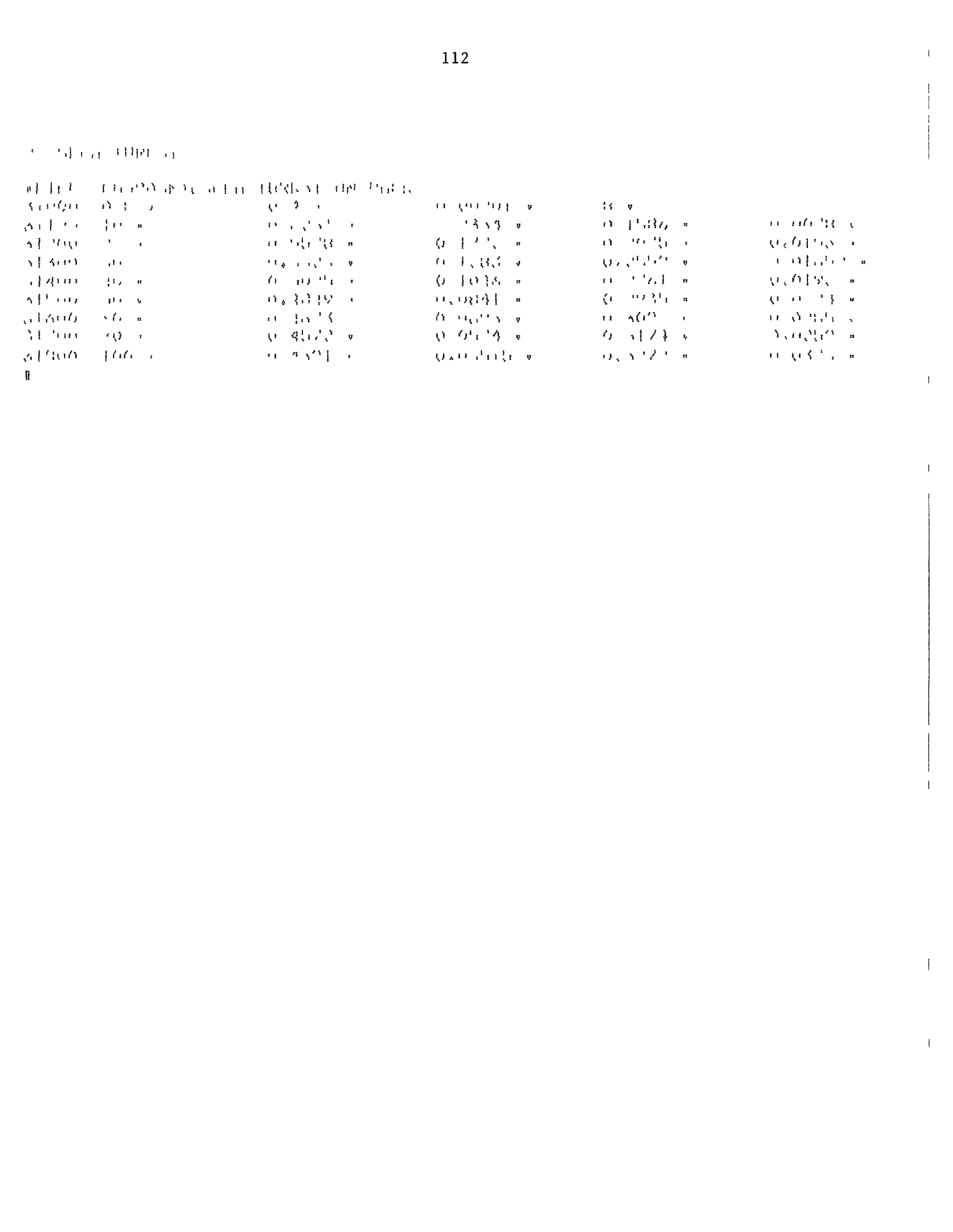


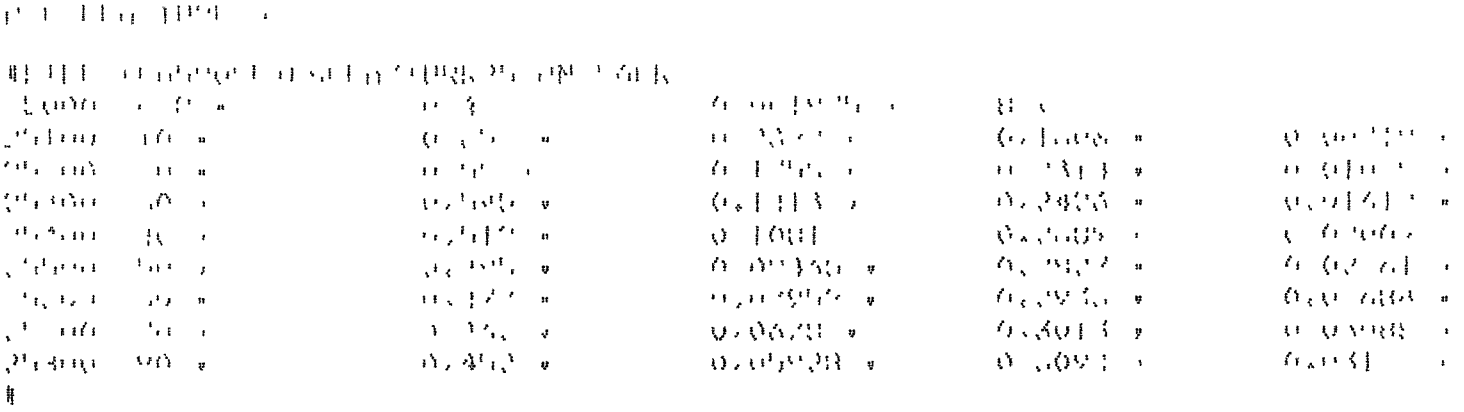


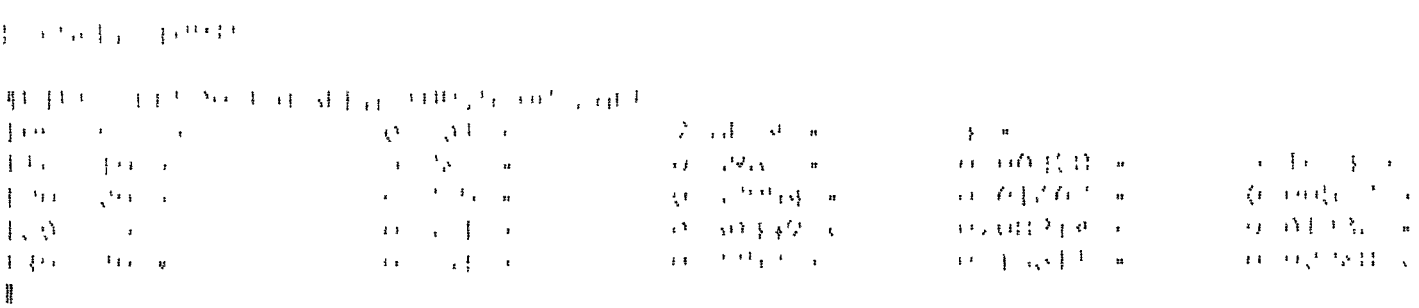
TAB LE:10

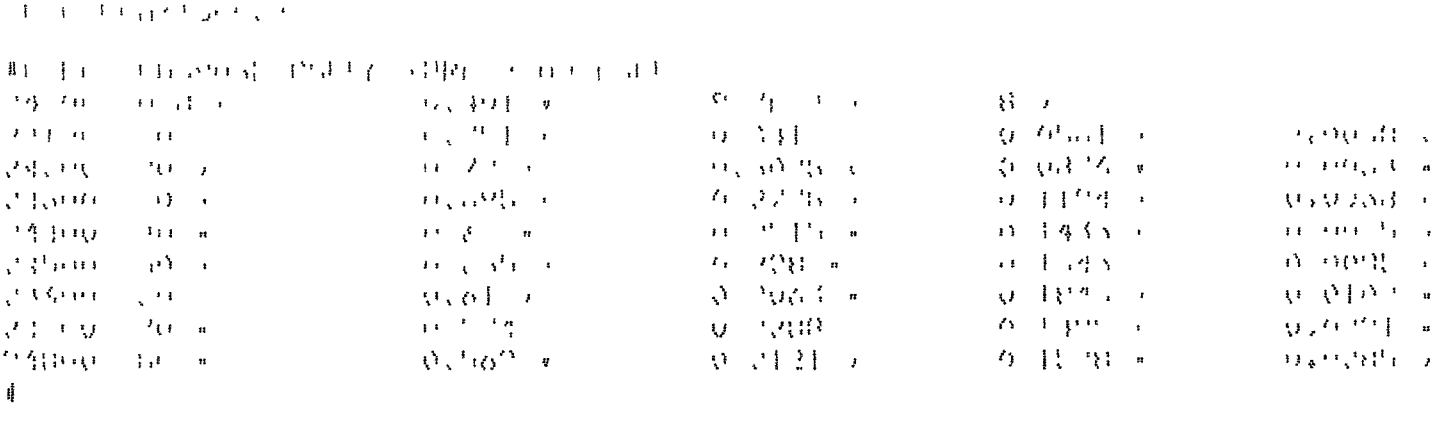












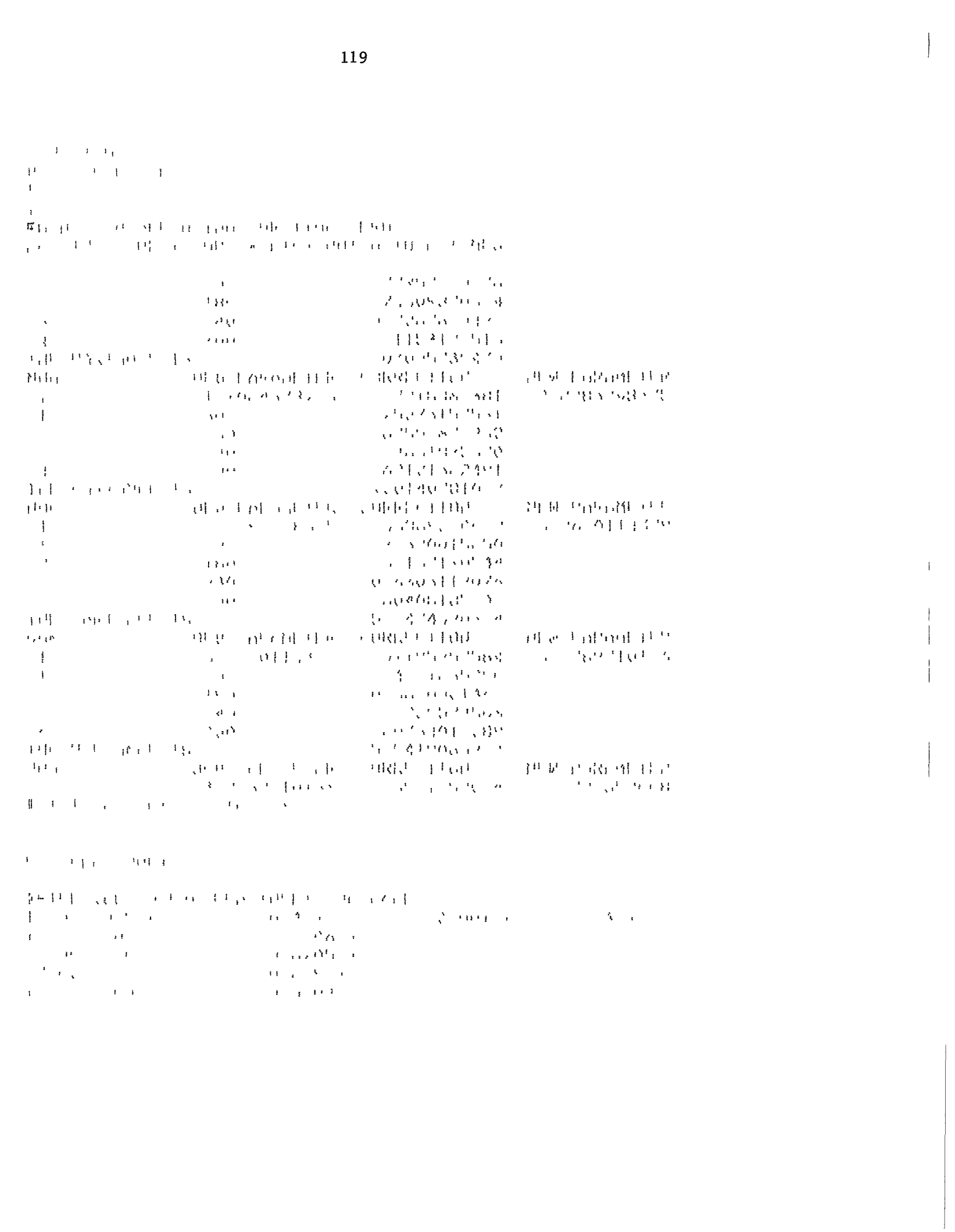
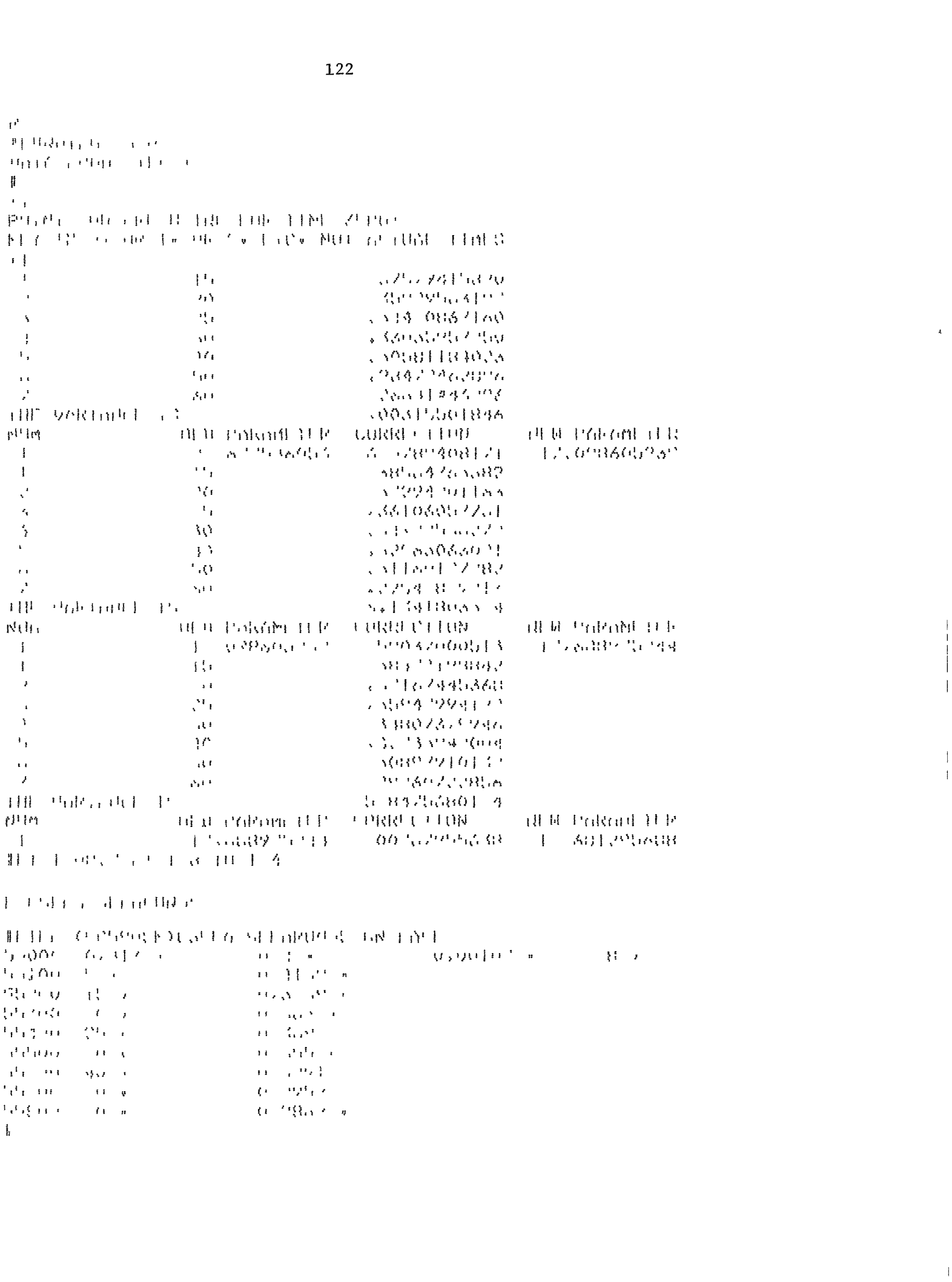
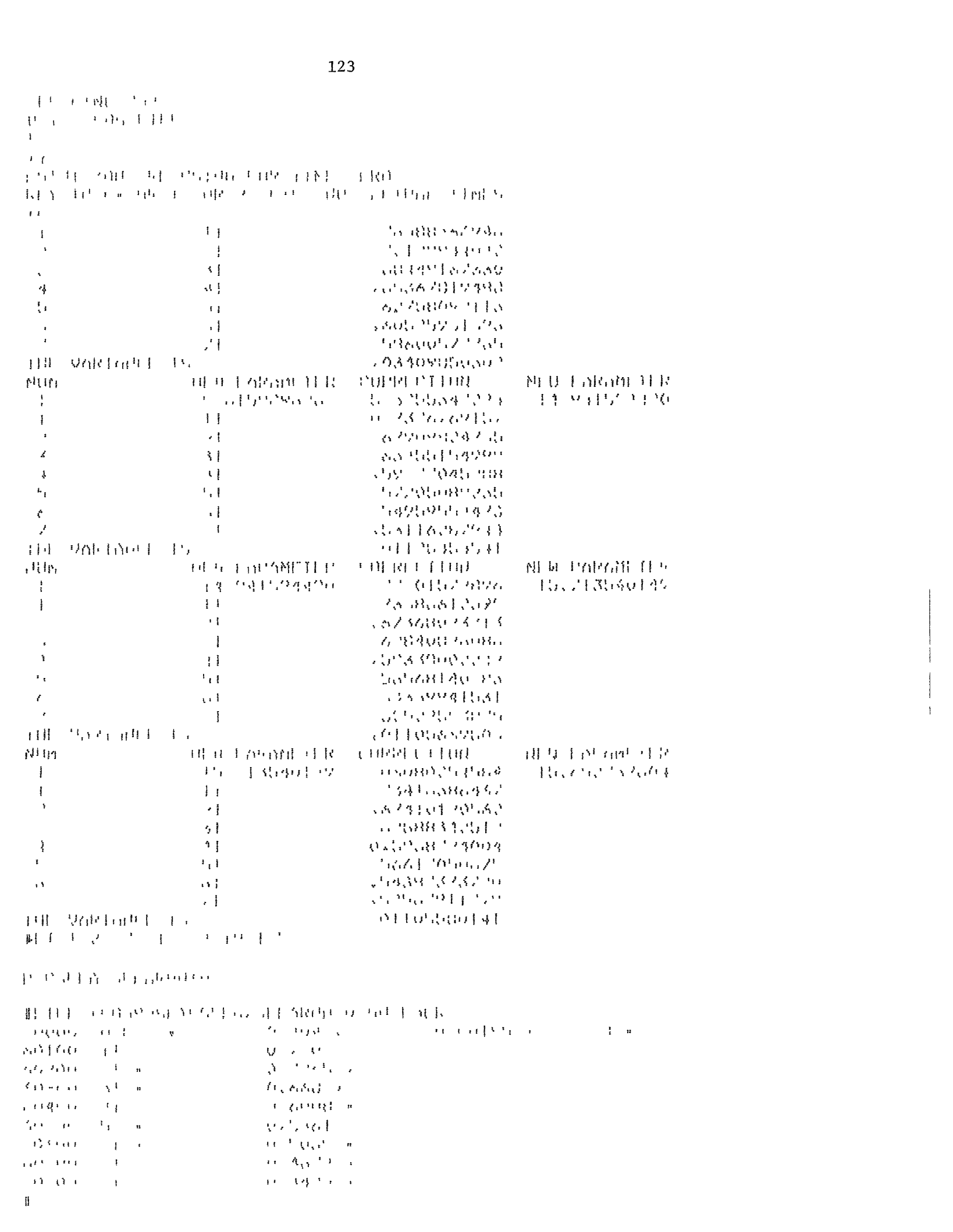


TABLE : 12





```
R
#RUNNING 7196
DATA FROM FILE ?
#?
?Y
POINT YOU ARE USING FOR TIME ZERO?
KEY IN 0, OR 1, OR 2, ETC, NOT ACTUAL TIMES
?1
 1                21                .05892053836
 2                31                .04132214659
 3                41                .02941075621
 4                51                .02114562022
 5                61                .01531114818
 6                71                .01114237059
THE VARIANCE IS                     2.14047774-4
NUM              OLD PARAMETER   CORRECTION      NEW PARAMETER
 1                5025.0307041    1096.2713317    6121.3020357
 1                21              .05444608340
 2                31              .03557126429
 3                41              .02367686924
 4                51              .01594877612
 5                61              .01082750000
 6                71              .00738916536
THE VARIANCE IS                     3.49837642-5
NUM              OLD PARAMETER   CORRECTION      NEW PARAMETER
 1                6121.3020357    108.72120501    6230.0232407
 1                21              .05402415848
 2                31              .03505121103
 3                41              .02317767740
 4                51              .01551250210
 5                61              .01046438699
 6                71              .00709598790
THE VARIANCE IS                     3.38884470-5
NUM              OLD PARAMETER   CORRECTION      NEW PARAMETER
 1                6230.0232407   -4.4513742936    6225.5718664
#ET=1;05.4 PT=2.0 IO=1.4


P CSEFA/SEFARUN14

#FILE (CG590SK)CSEFA/SEFARUN14 ON PACK
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14100  11 ,             0.0859 ,
14200  21 ,             0.0586 ,
14300  31 ,             0.0364 ,
14400  41 ,             0.0216 ,
14500  51 ,             0.0133 ,
14600  61 ,             0.0087 ,
14700  71 ,             0.0063 ,
#
```

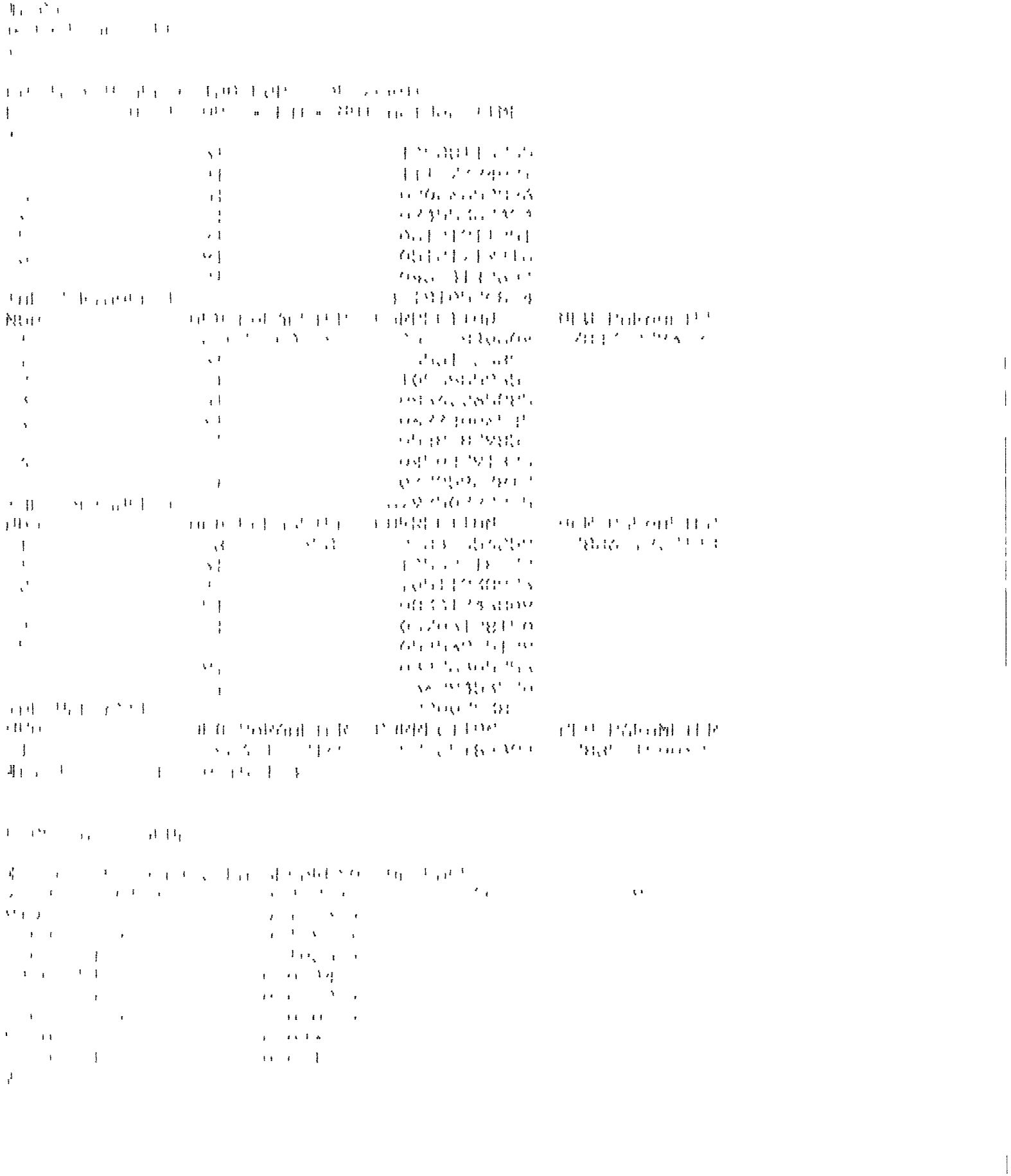

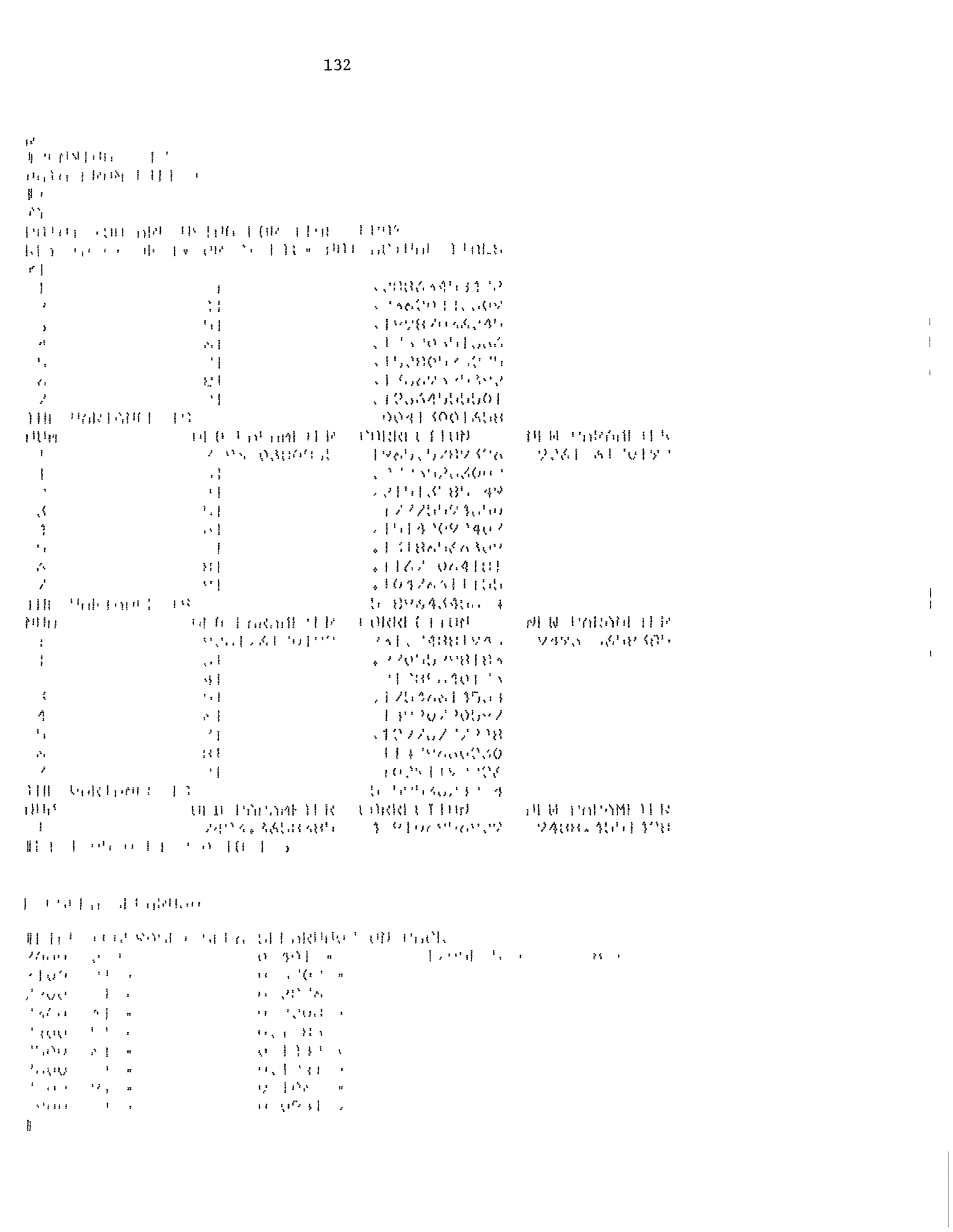

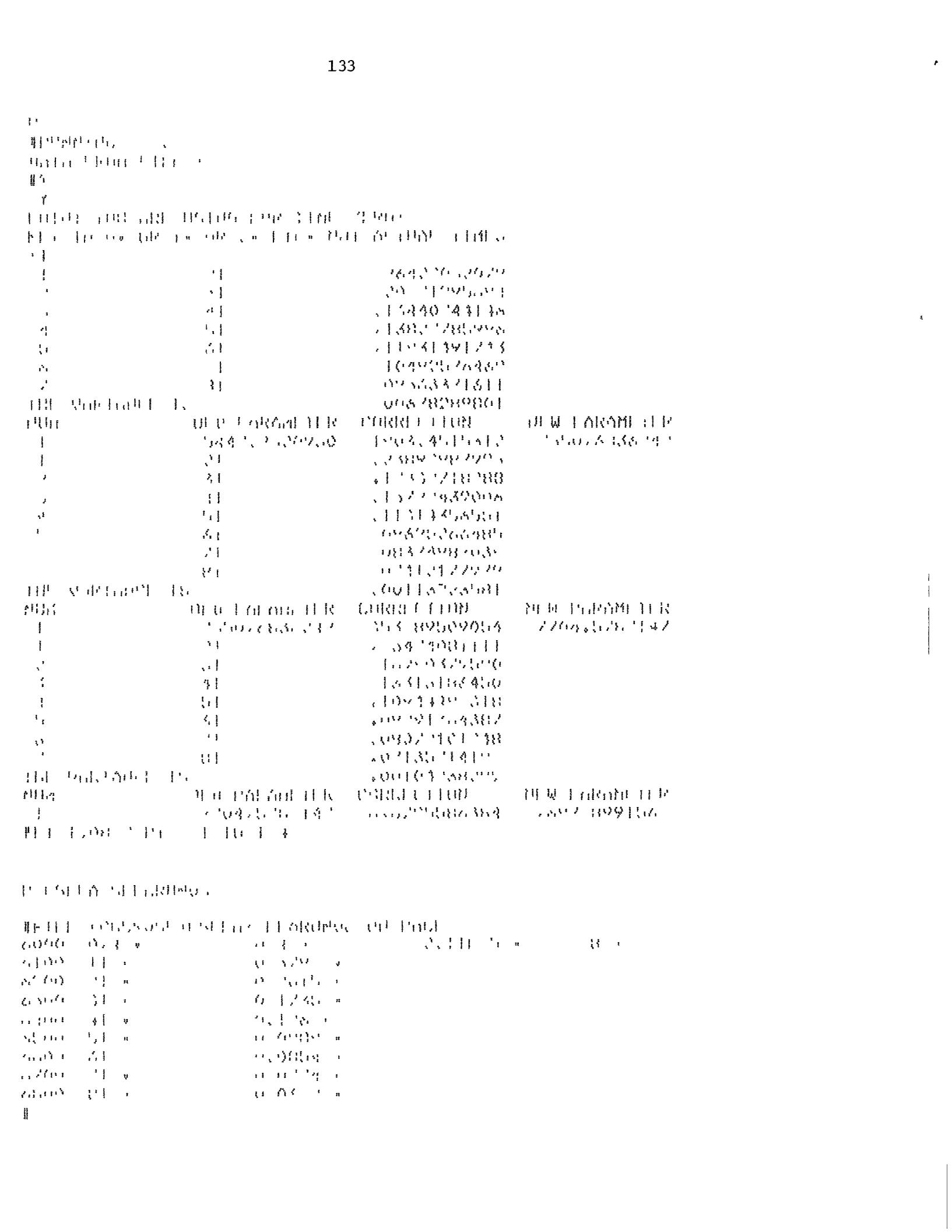

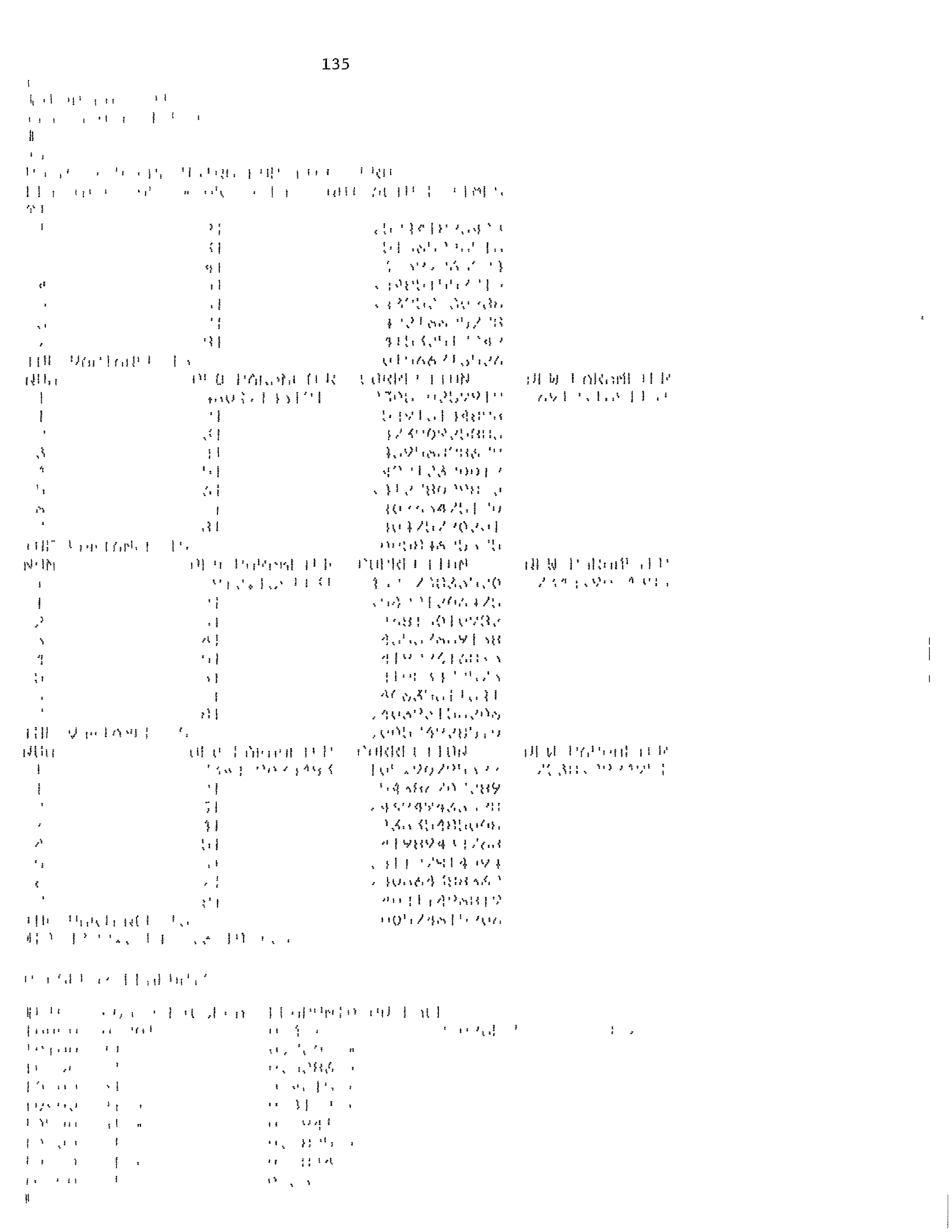

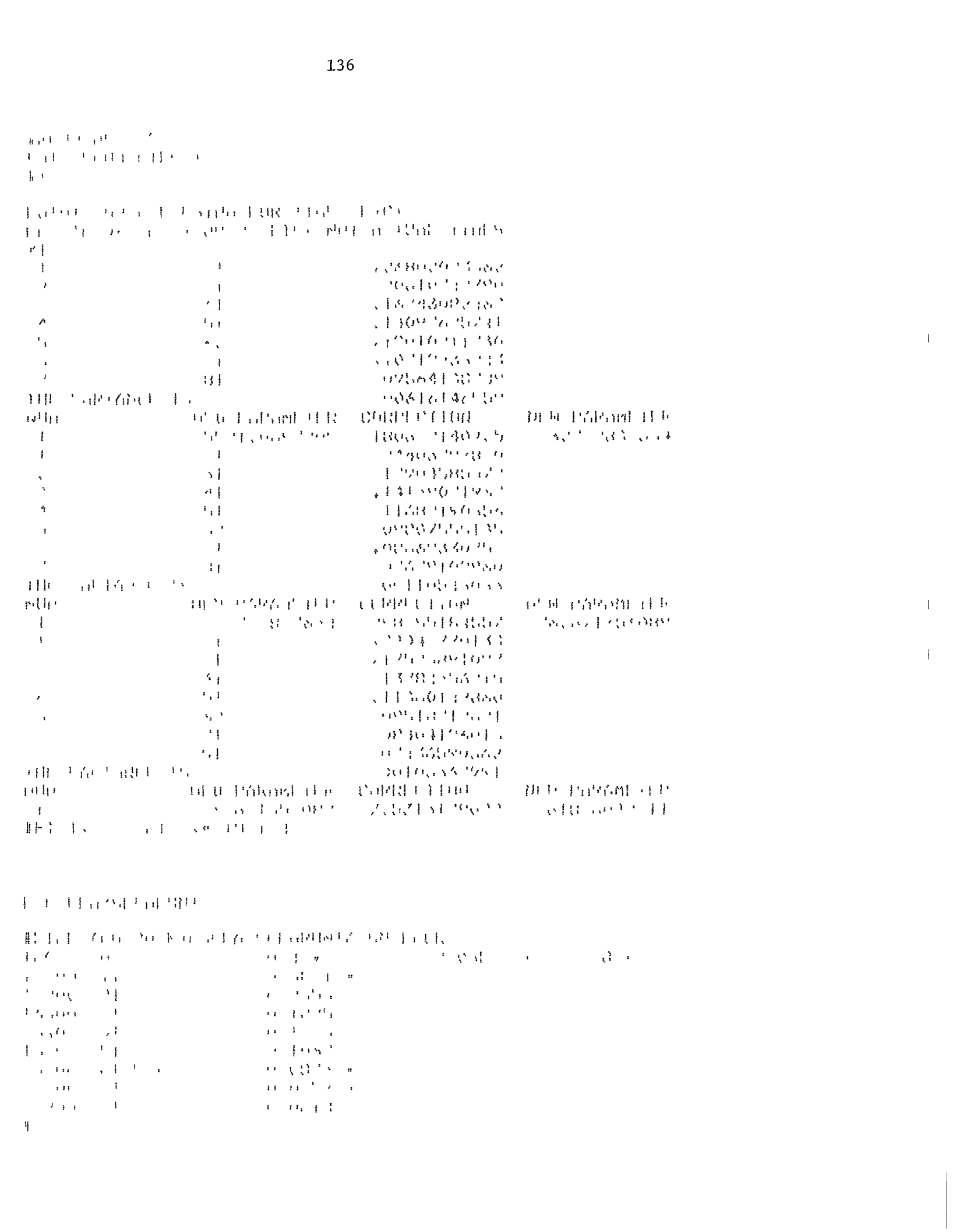

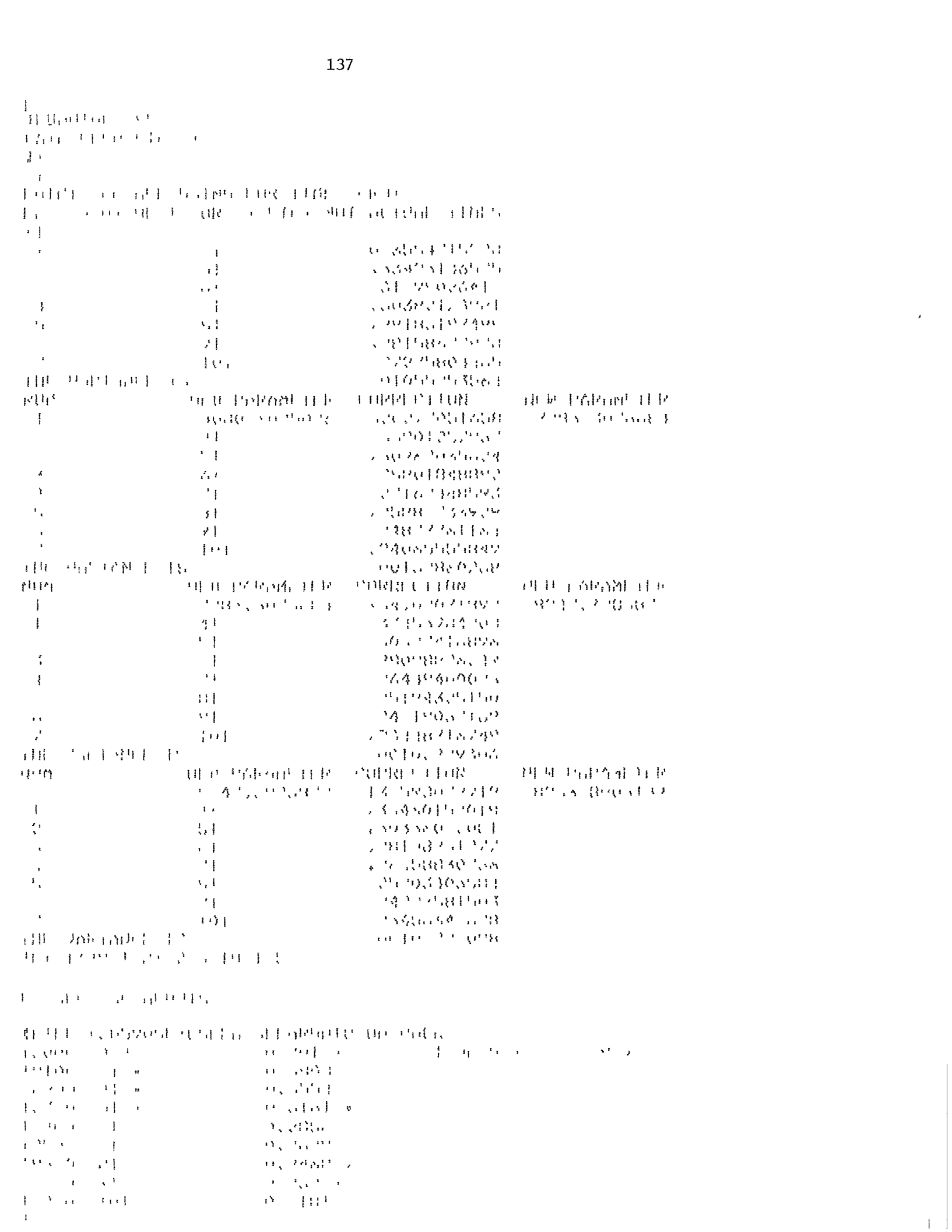

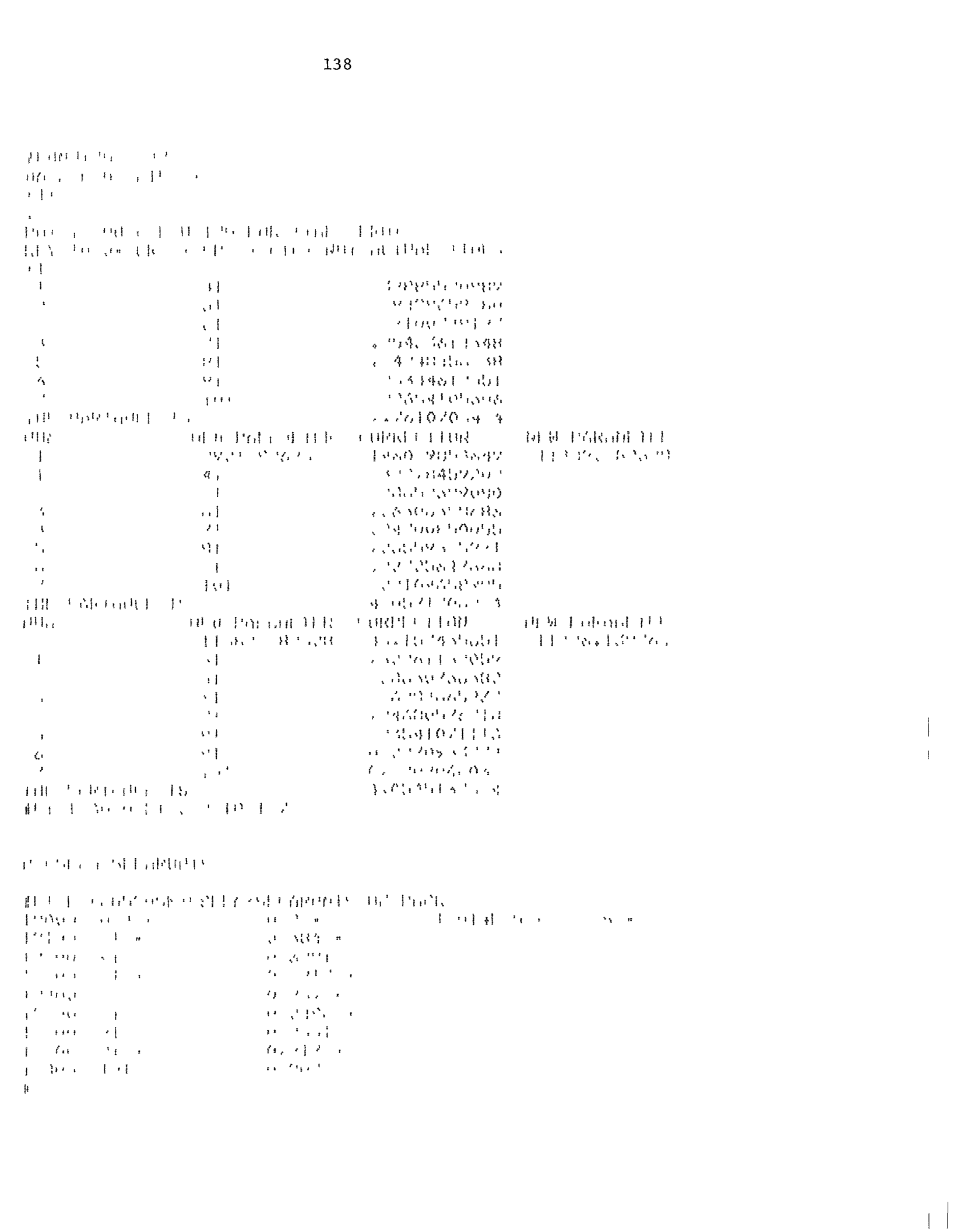

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P CSEFA/SEFARUN23

#FILE (CG590SK)CSEFA/SEFARUN23 ON PACK
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23200  31 ,             0.3232 ,
23300  41 ,             0.2043 ,
23400  51 ,             0.1296 ,
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23700  81 ,             0.0318 ,
23800  91 ,             0.0218 ,
#
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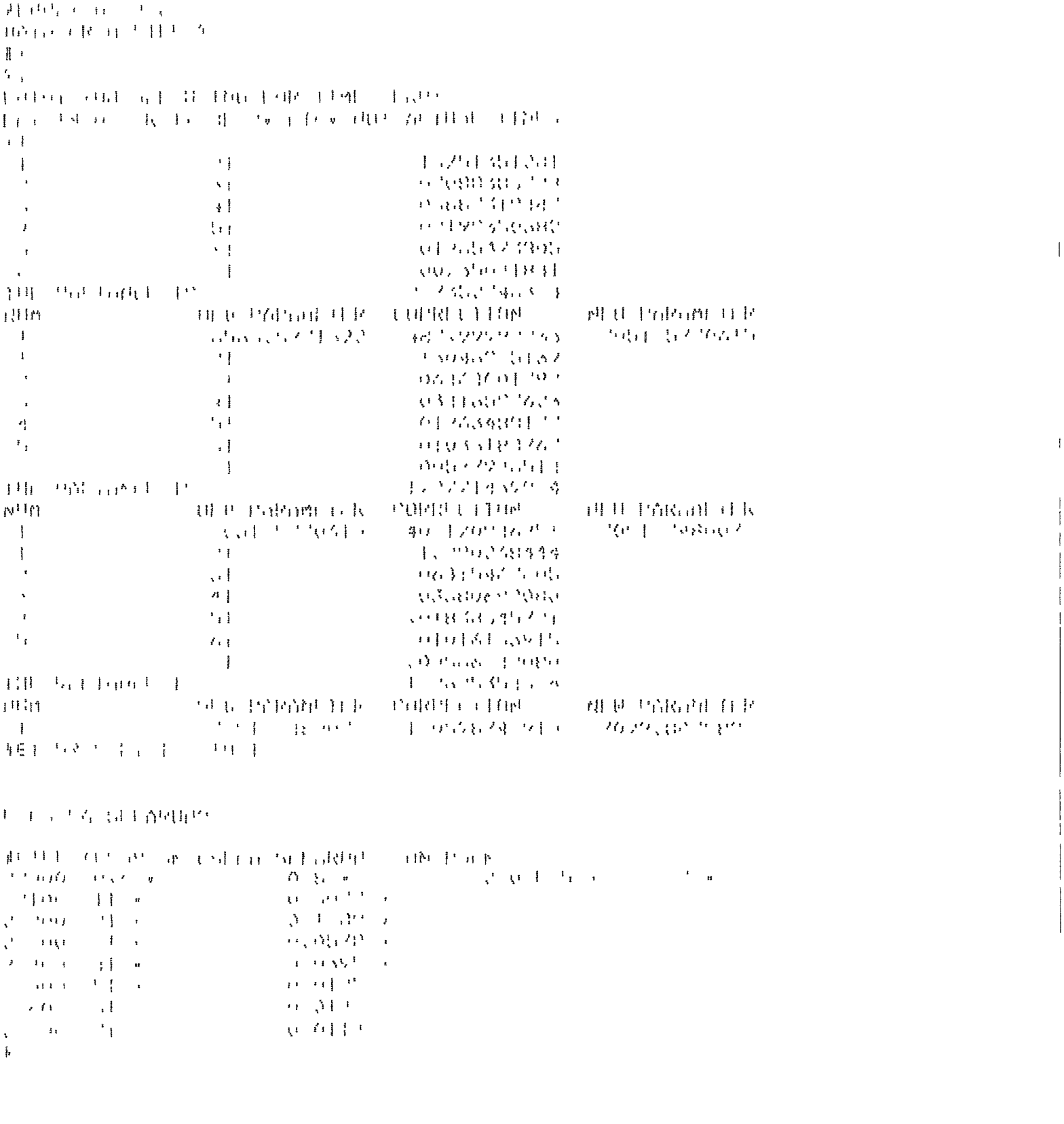
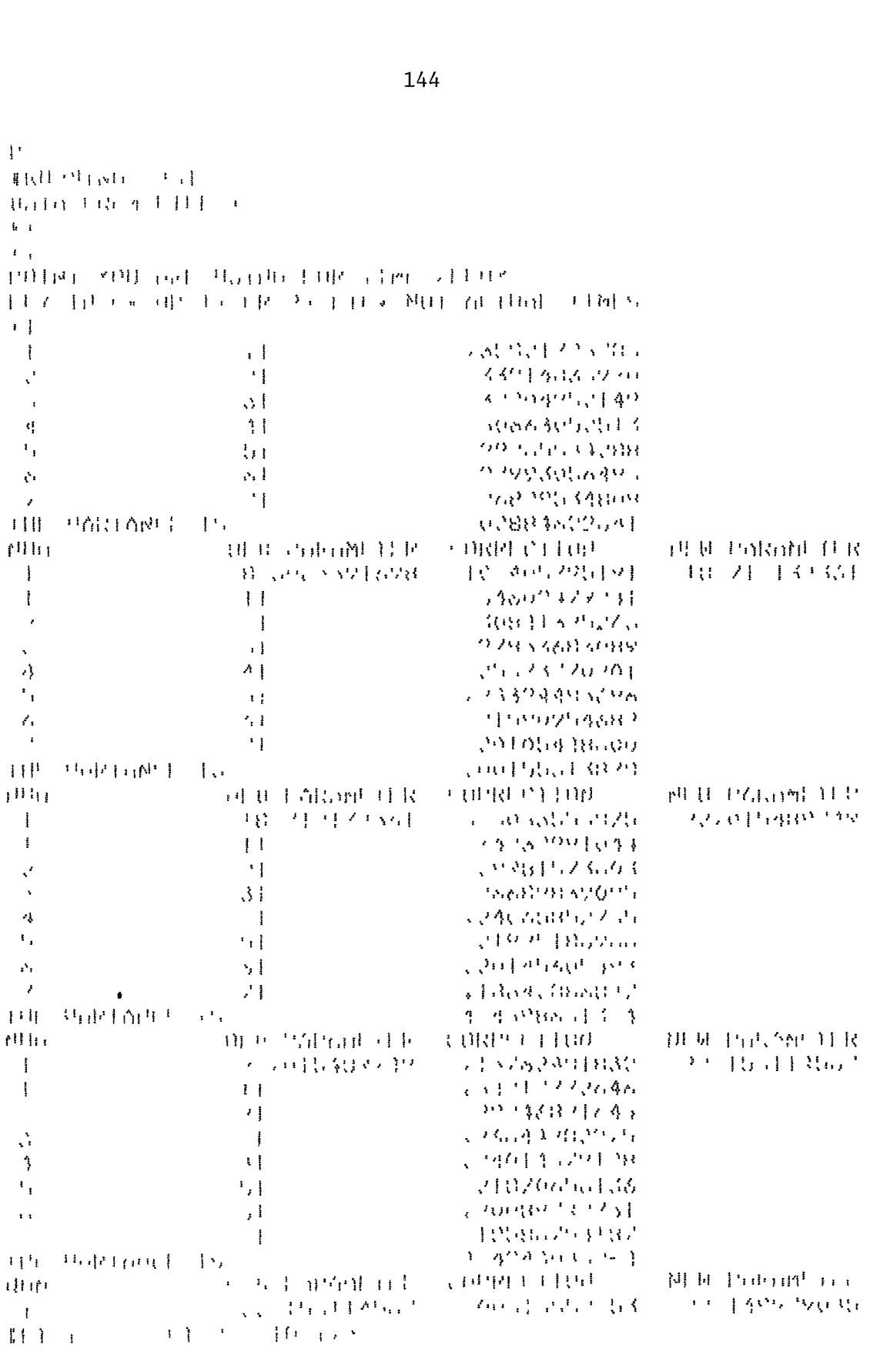


TABLE:13



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F CSEFA/SEFARUN78

#FILE (CG590SK)CSEFA/SEFARUN78 ON PACK
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78100  6 ,             0.3686 ,
78200  11 ,            0.3484 ,
78300  21 ,            0.31 ,
78400  31 ,            0.2755 ,
78500  41 ,            0.2438 ,
78600  51 ,            0.2179 ,
78700  61 ,            0.1958 ,
78800  71 ,            0.1728 ,
#
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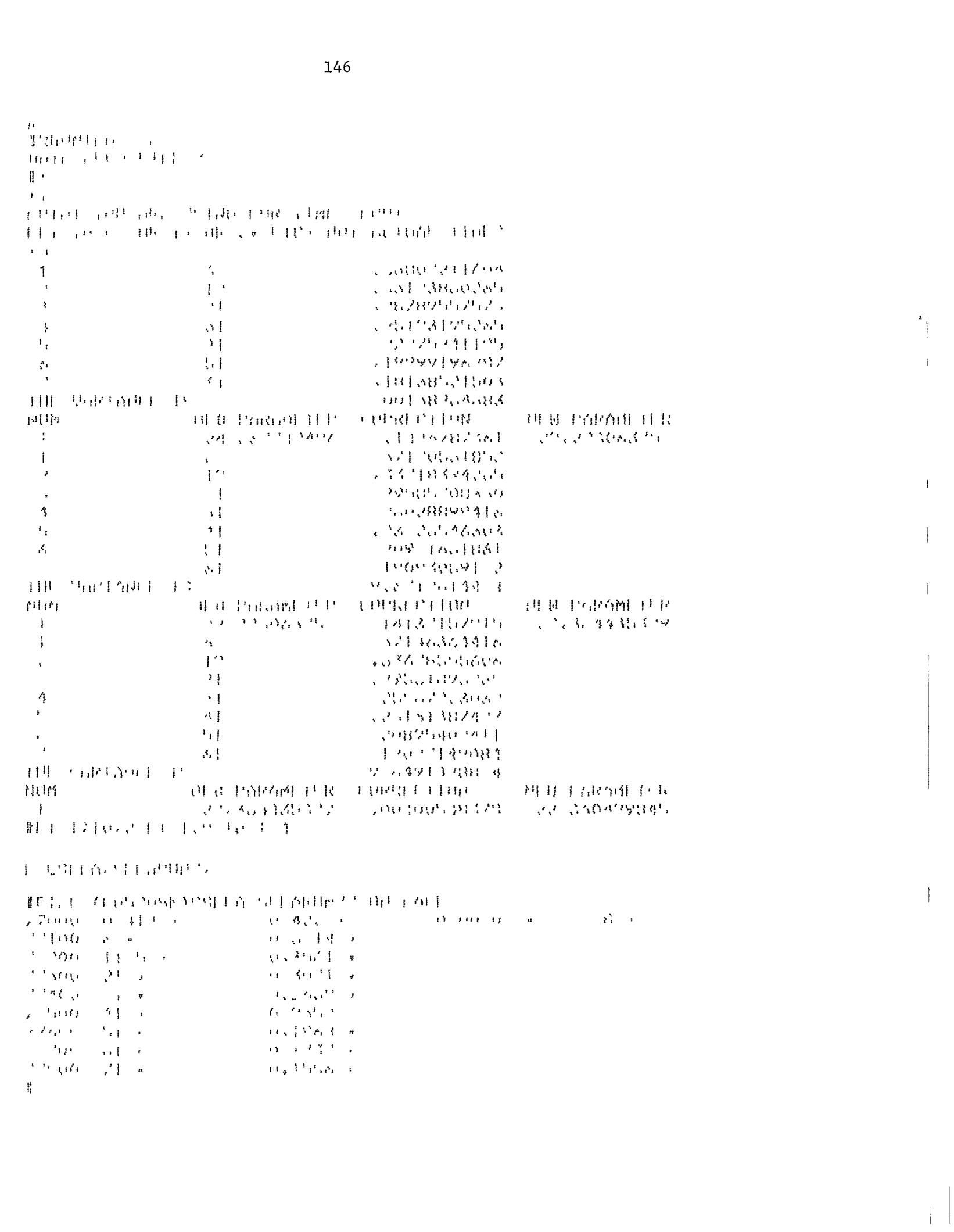

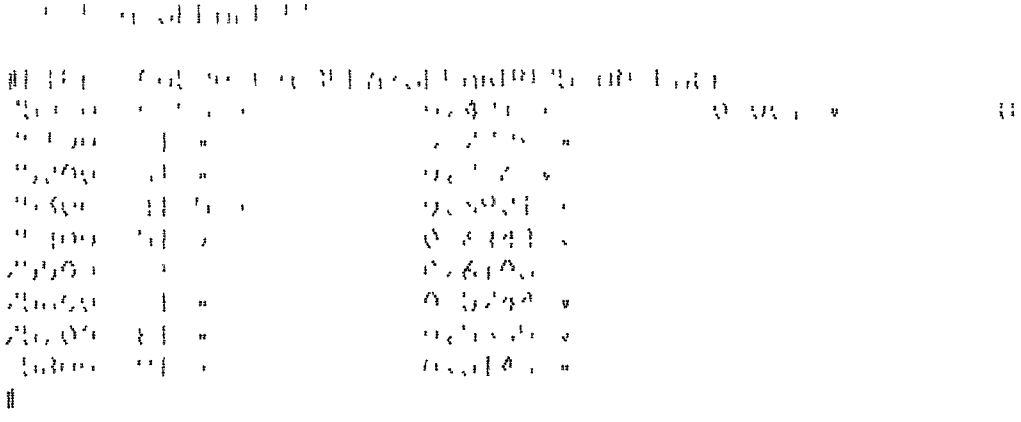

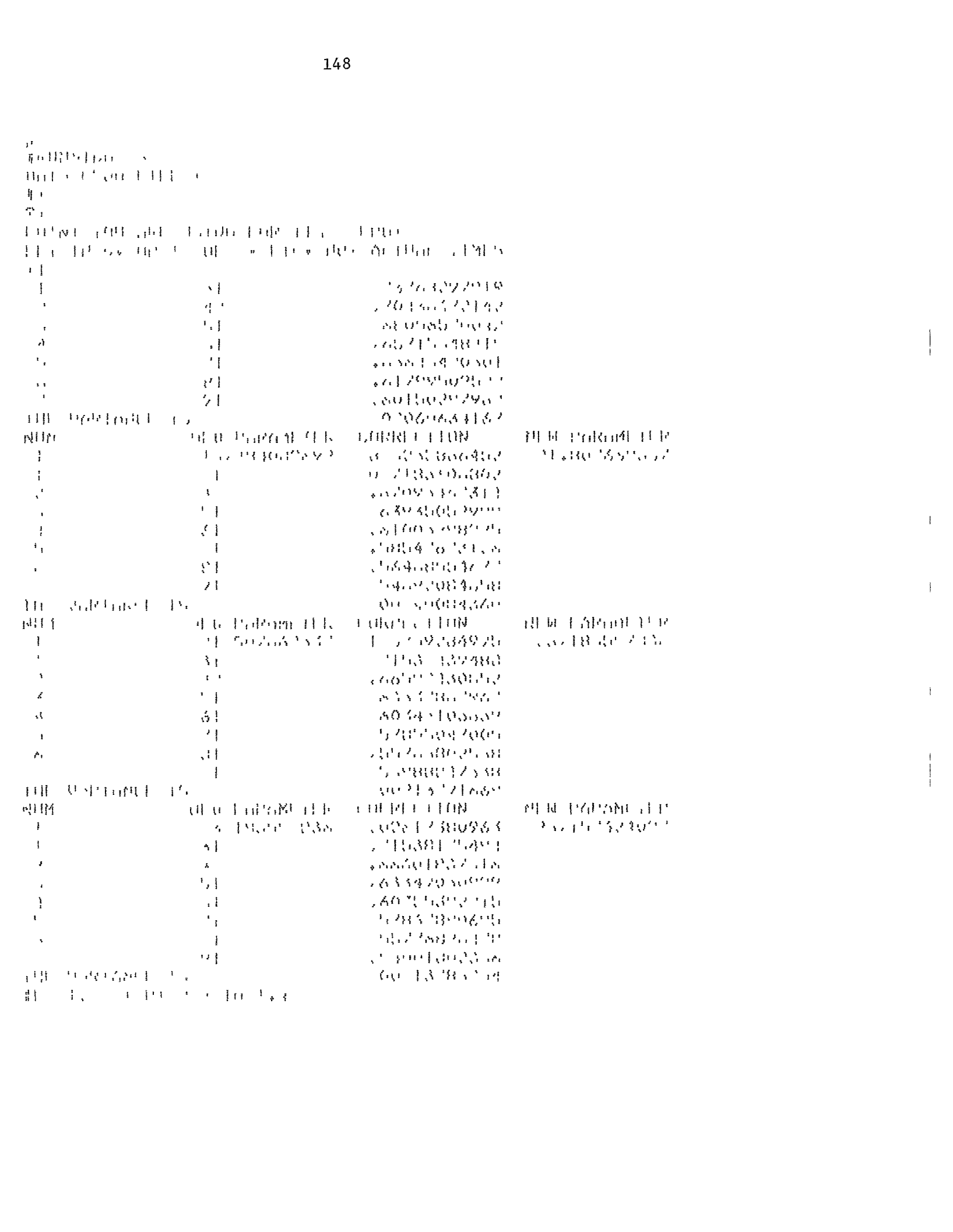

APPENDIX 4

Figure A1. Chromatogram of diphenyl sulfide

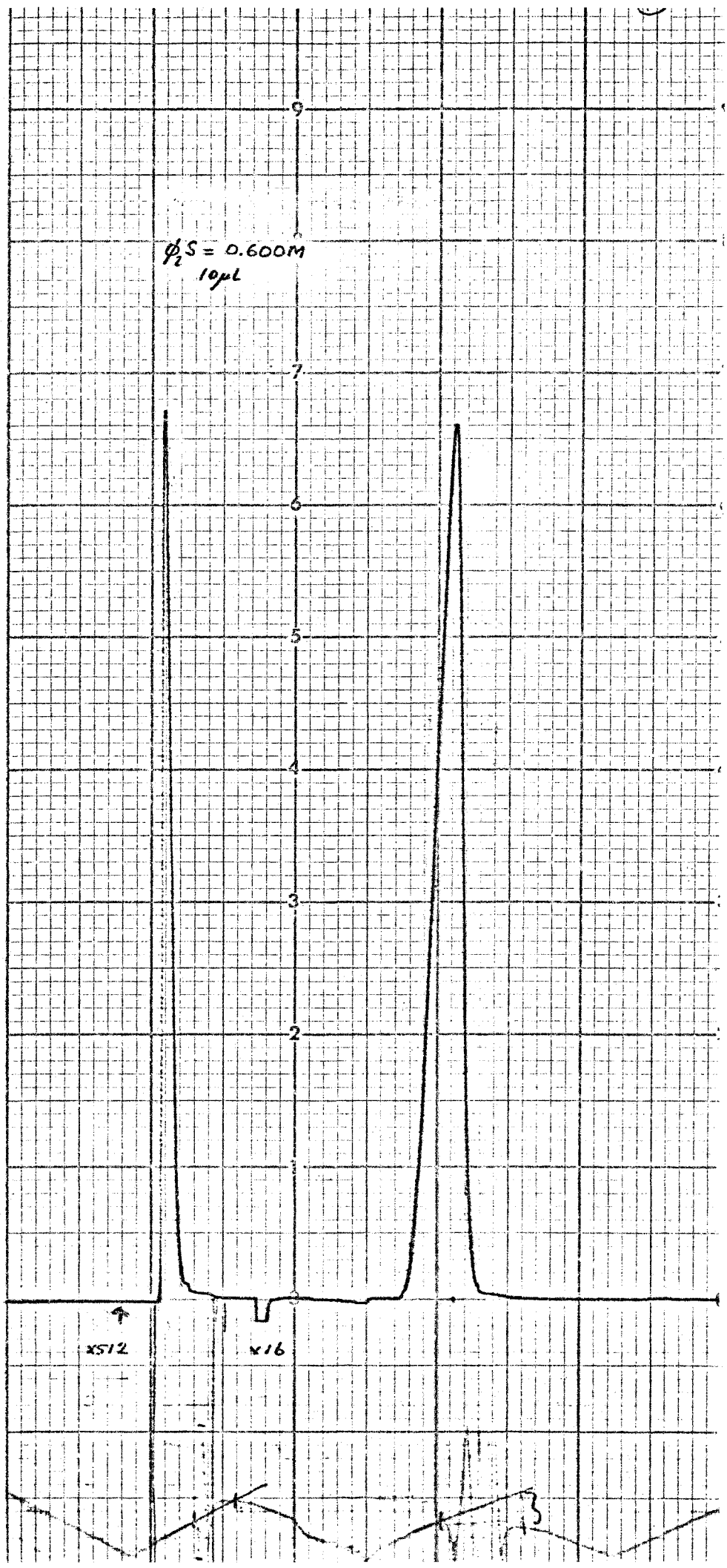
ϕ_2S = 0.600M
10μL
9
7
6
5
4
3
2
1
x512
x16

Figure A2. Chromatogram of diphenyl sulfoxide.

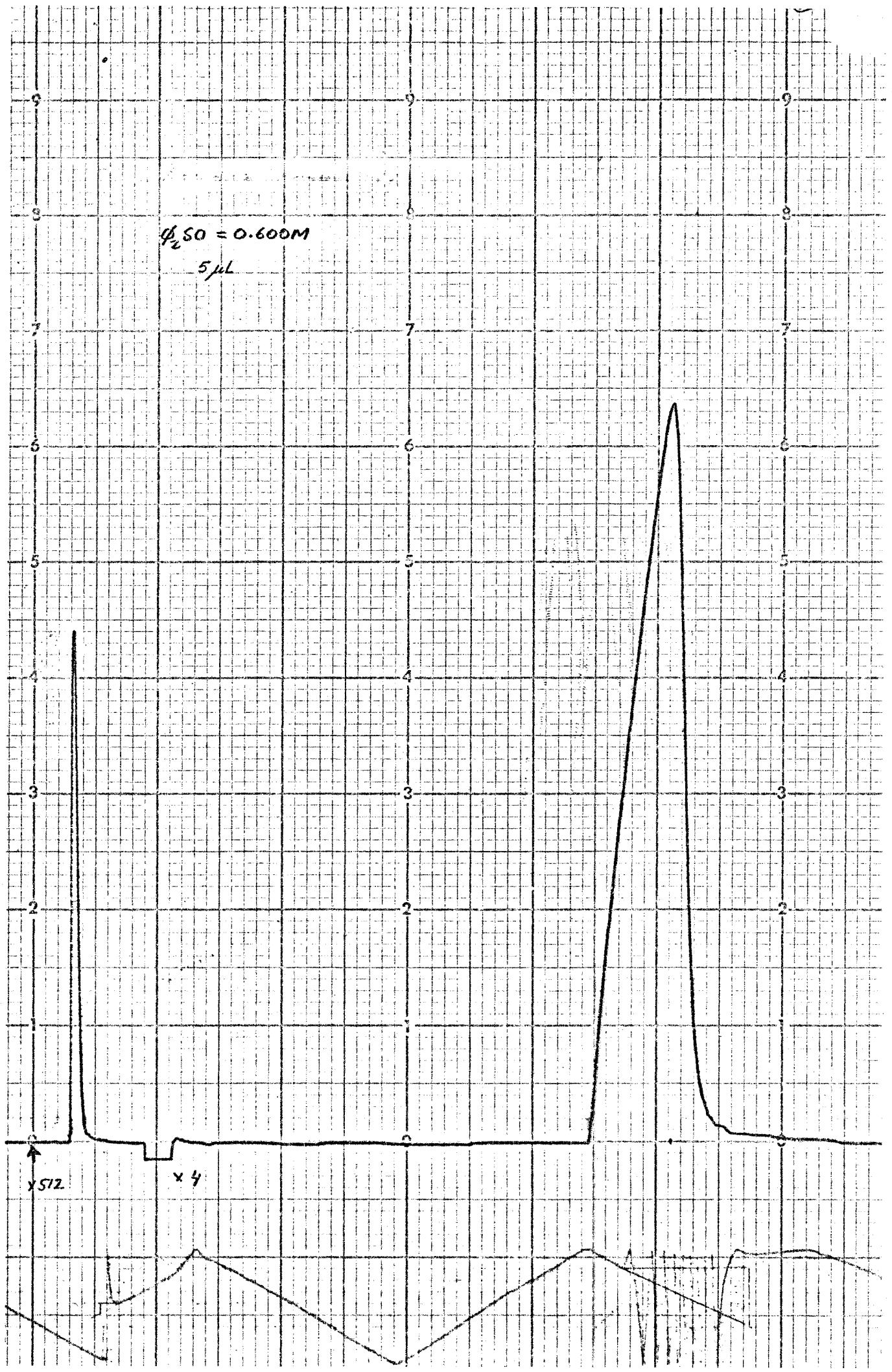
$\phi_2SO = 0.600M$
5 µL
x512
x 4

Figure A3. Chromatogram of diphenyl sulfone

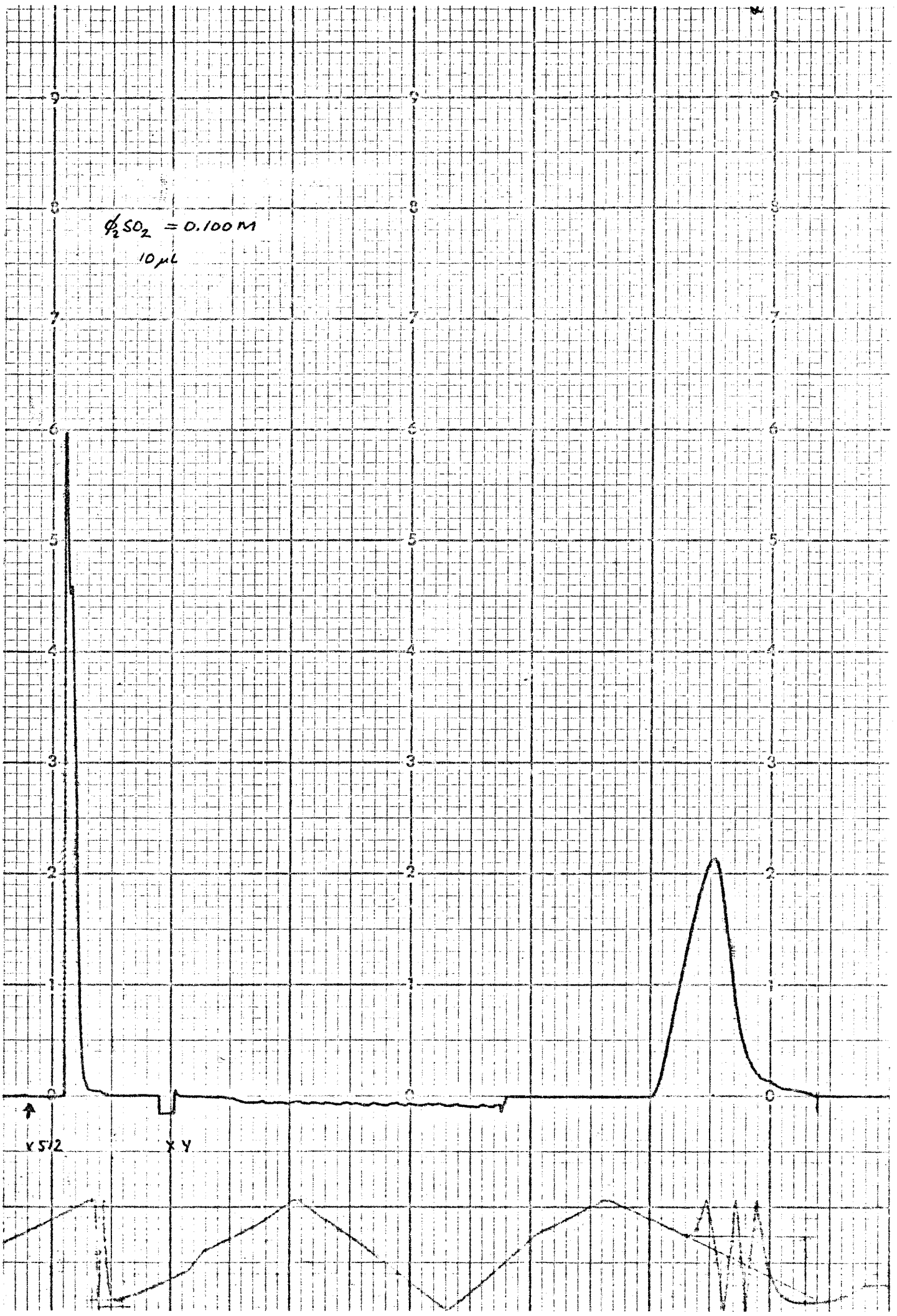
ϕ_2SO_2 = 0.100 M
10 μL
X 512
X Y

Figure A4. Chromatogram of mixture of diphenyl sulfoxide and diphenyl sulfone.

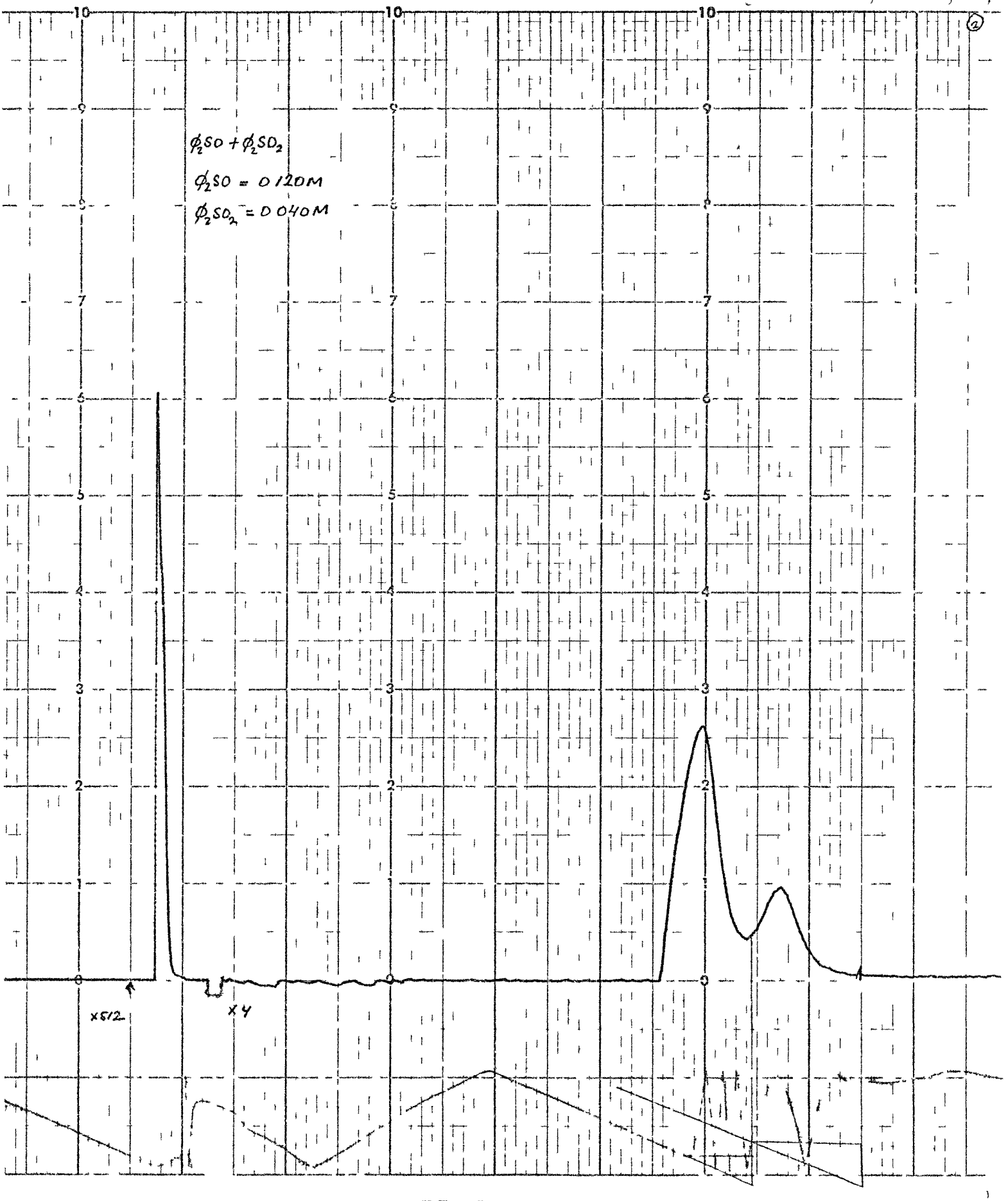

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Figure A5. Chromatogram of mixture of diphenyl sulfide, diphenyl sulfoxide and diphenyl sulfone.

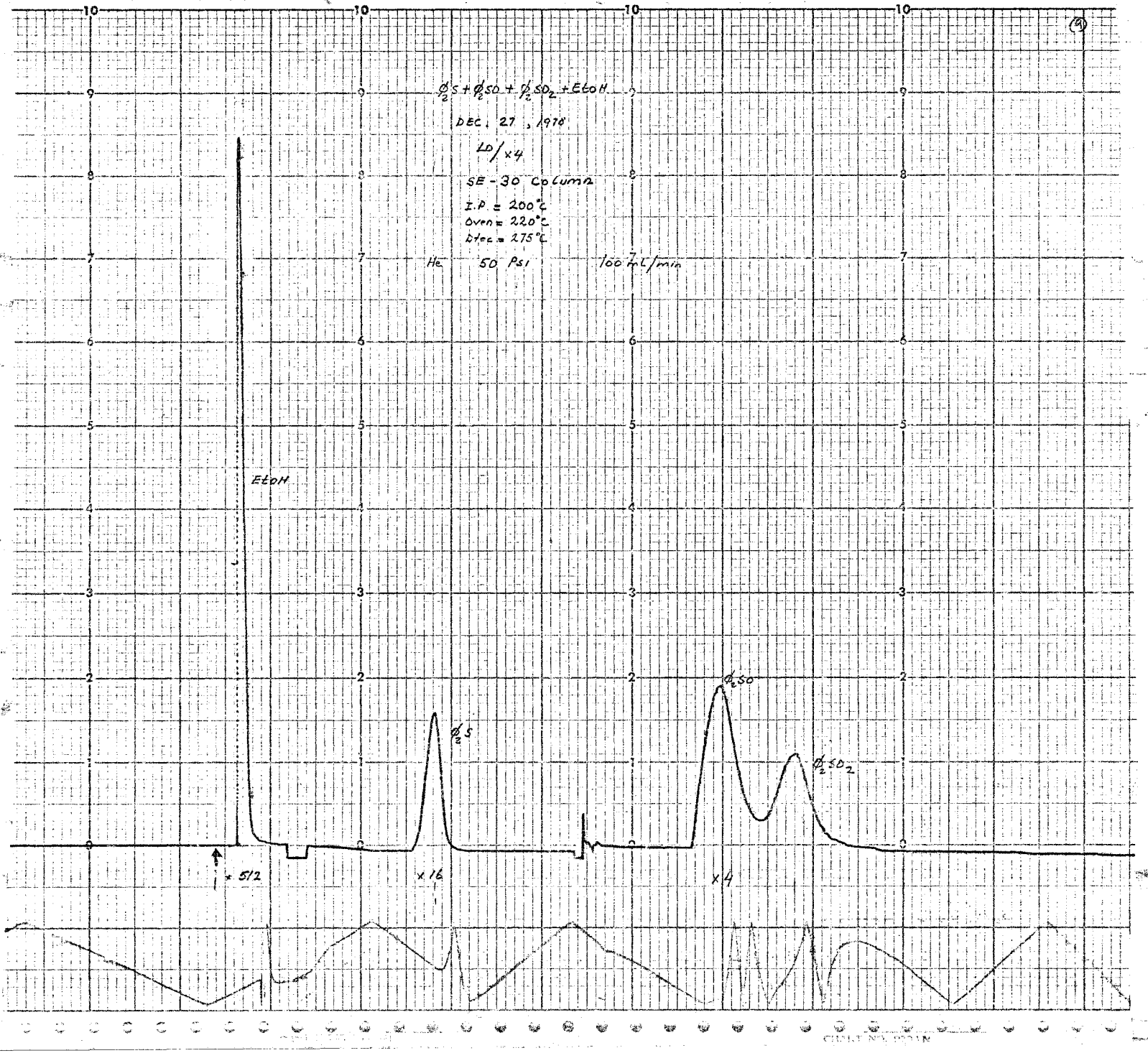

$\phi_2S + \phi_2SO + \phi_2SO_2 + EtOH$
DEC. 27, 1978
LD/×4
SE-30 Column
I.P. = 200°C
Oven = 220°C
Dtec = 275°C
He 50 Psi
100 mL/min
EtOH
ϕ_2S
ϕ_2SO
ϕ_2SO_2
× 512
× 16
× 4

Figure A6. Sample chromatogram of diphenyl sulfide, diphenyl sulfoxide and diphenyl sulfone in the presence of triphenyl phosphine.

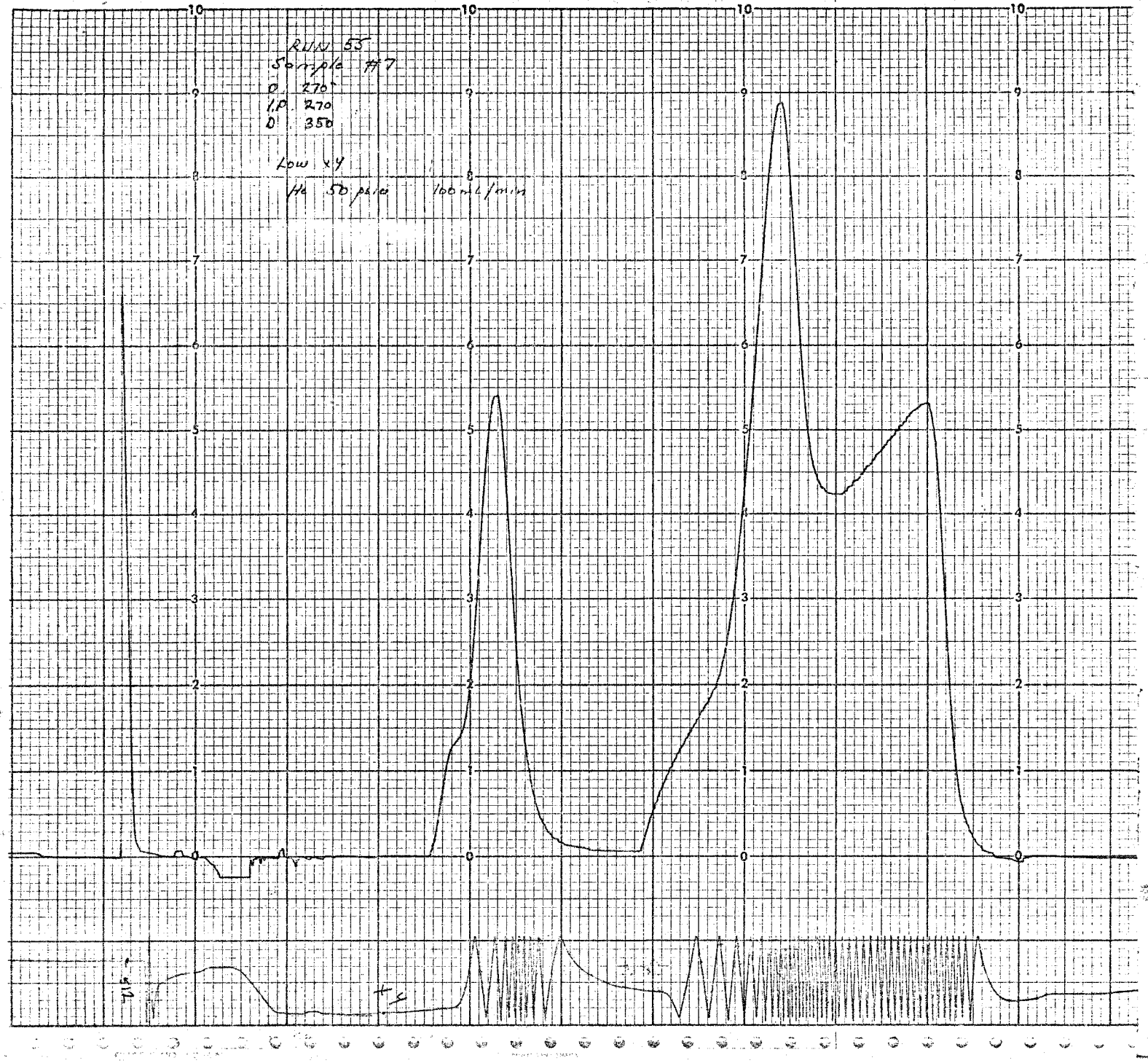
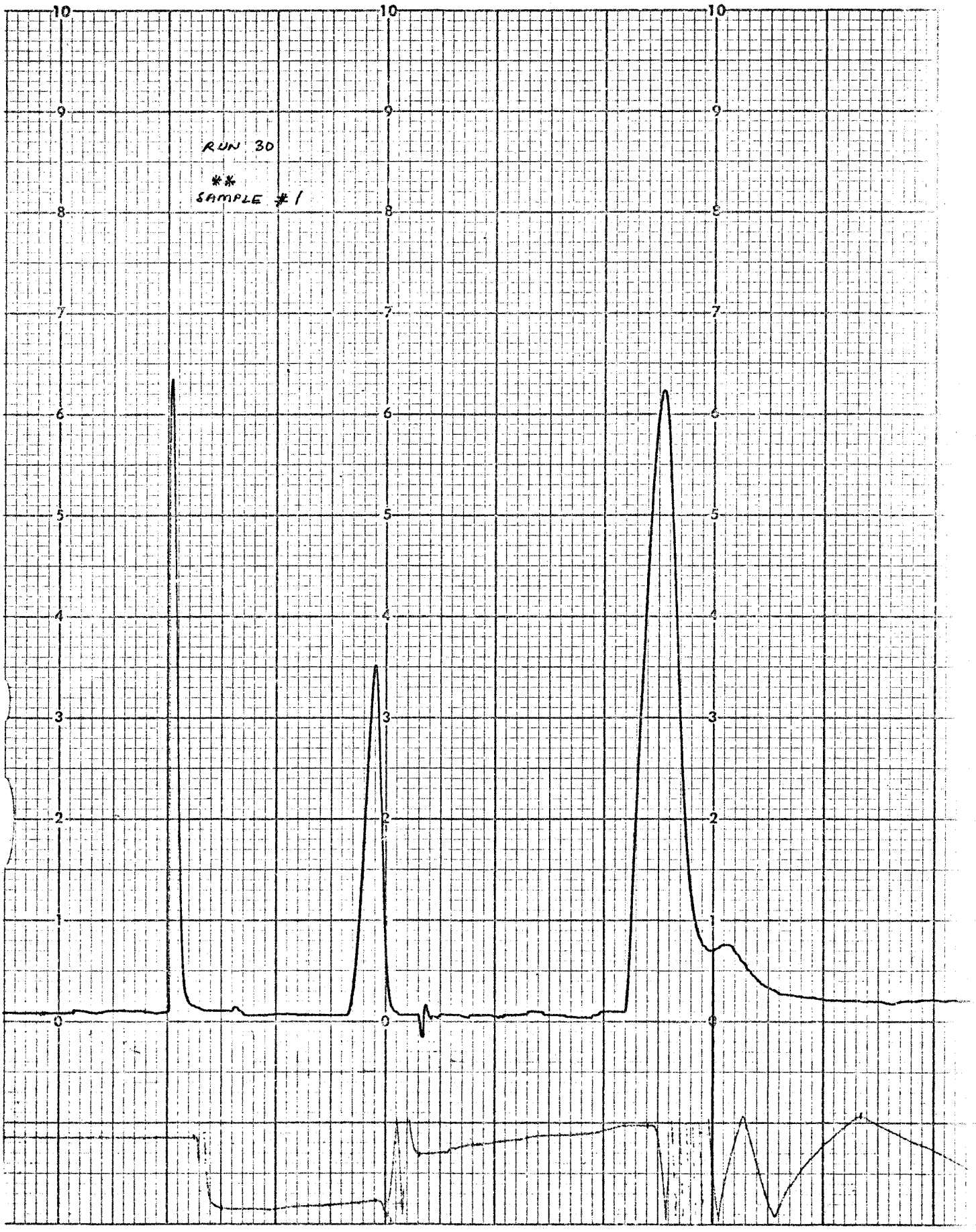

RUN 53
Sample #7
D 270°
I.P. 270
D 350
Low x4
1/4 50 psia 100 ml/min

Figure A7. Chromatogram of zero point sample of Run 30.


RUN 30
**
SAMPLE #1

APPENDIX 5

Figure A8. UV spectrum of diphenyl sulfide

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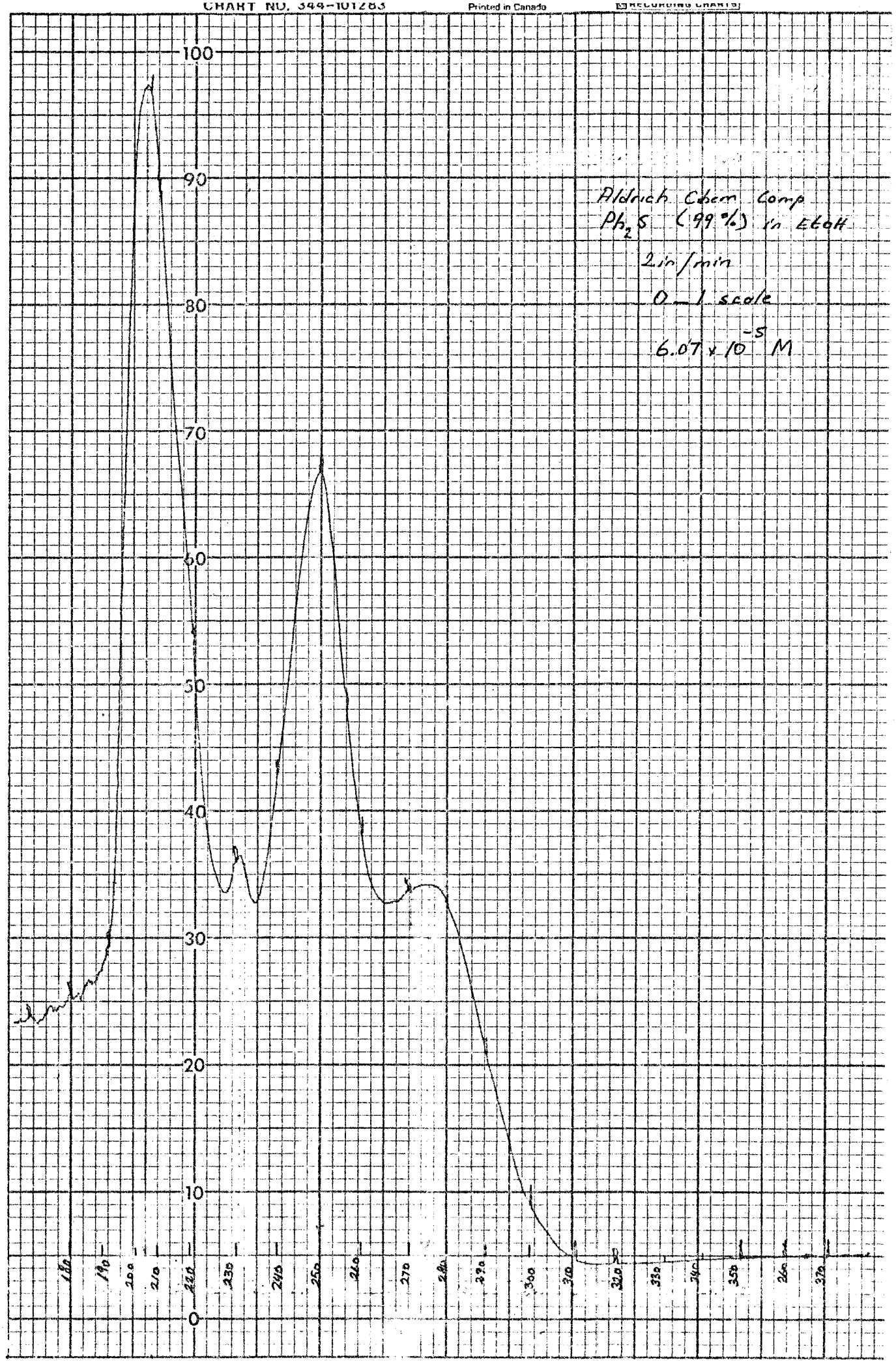


Figure A9. UV spectrum of diphenyl sulfoxide.

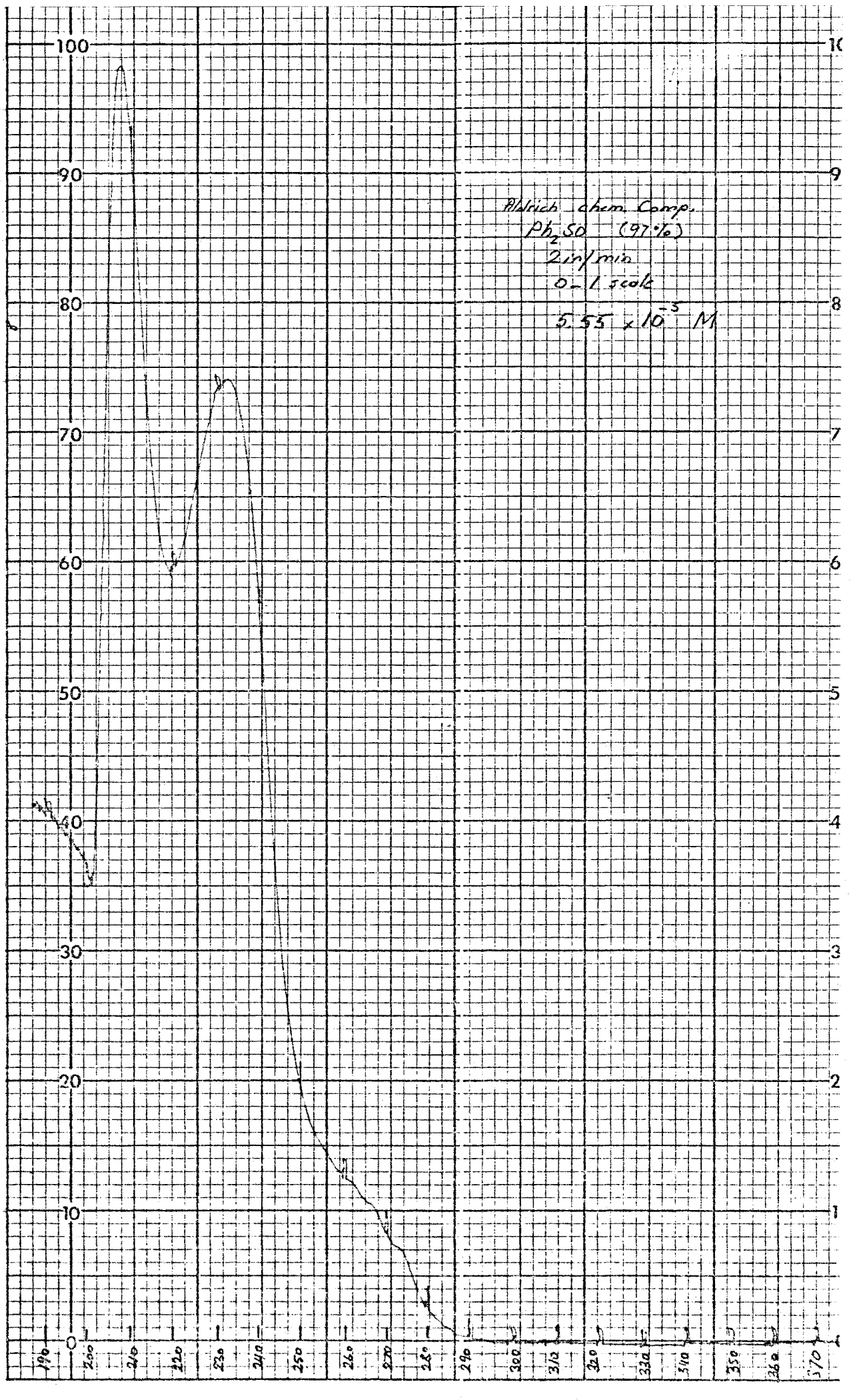

Aldrich chem. Comp.
Ph_2SO (97%)
2 in/min
0-1 scale
5.55×10^{-5} M
100
90
80
70
60
50
40
30
20
10
0
190
200
210
220
230
240
250
260
270
280
290
300
310
320
330
340
350
360
370

Figure A10. UV spectrum of diphenyl sulfone.

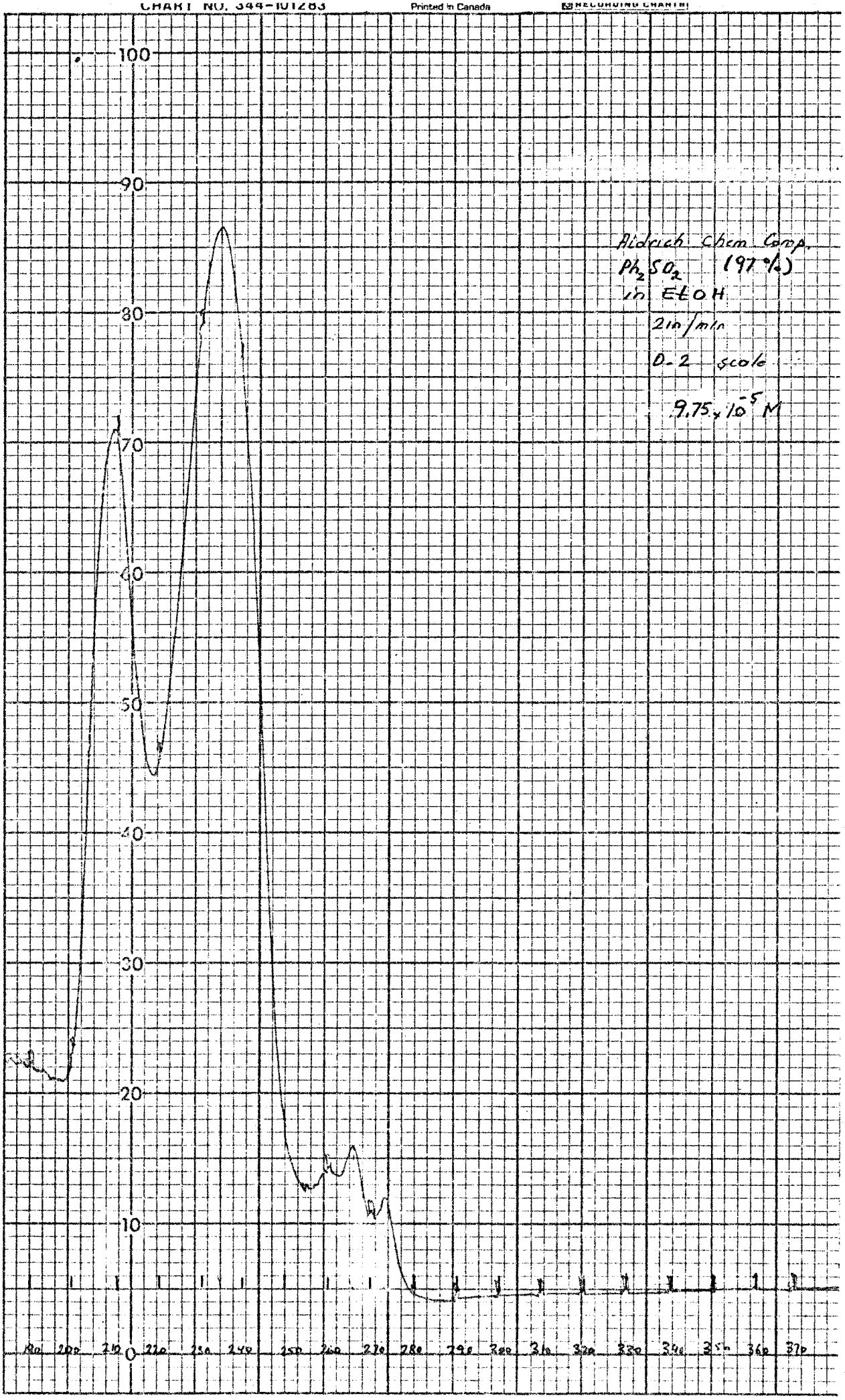
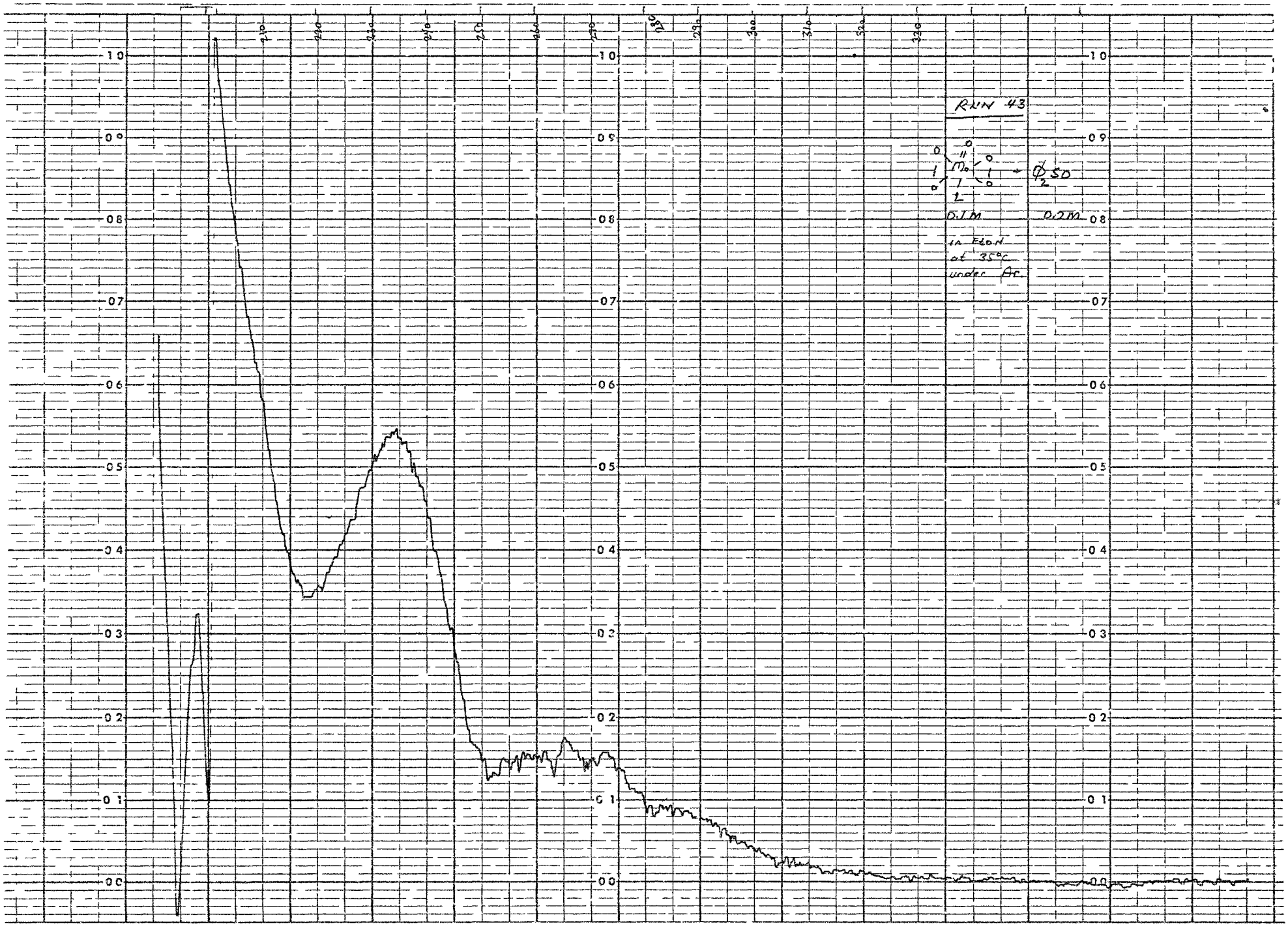
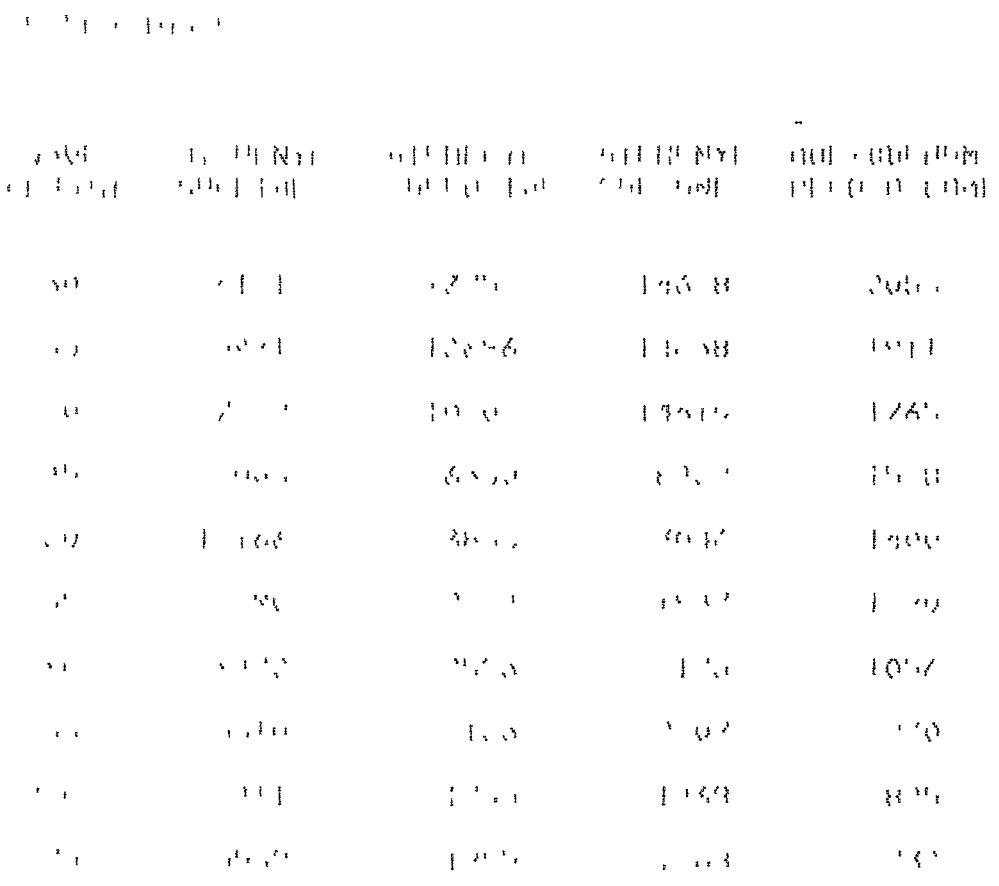


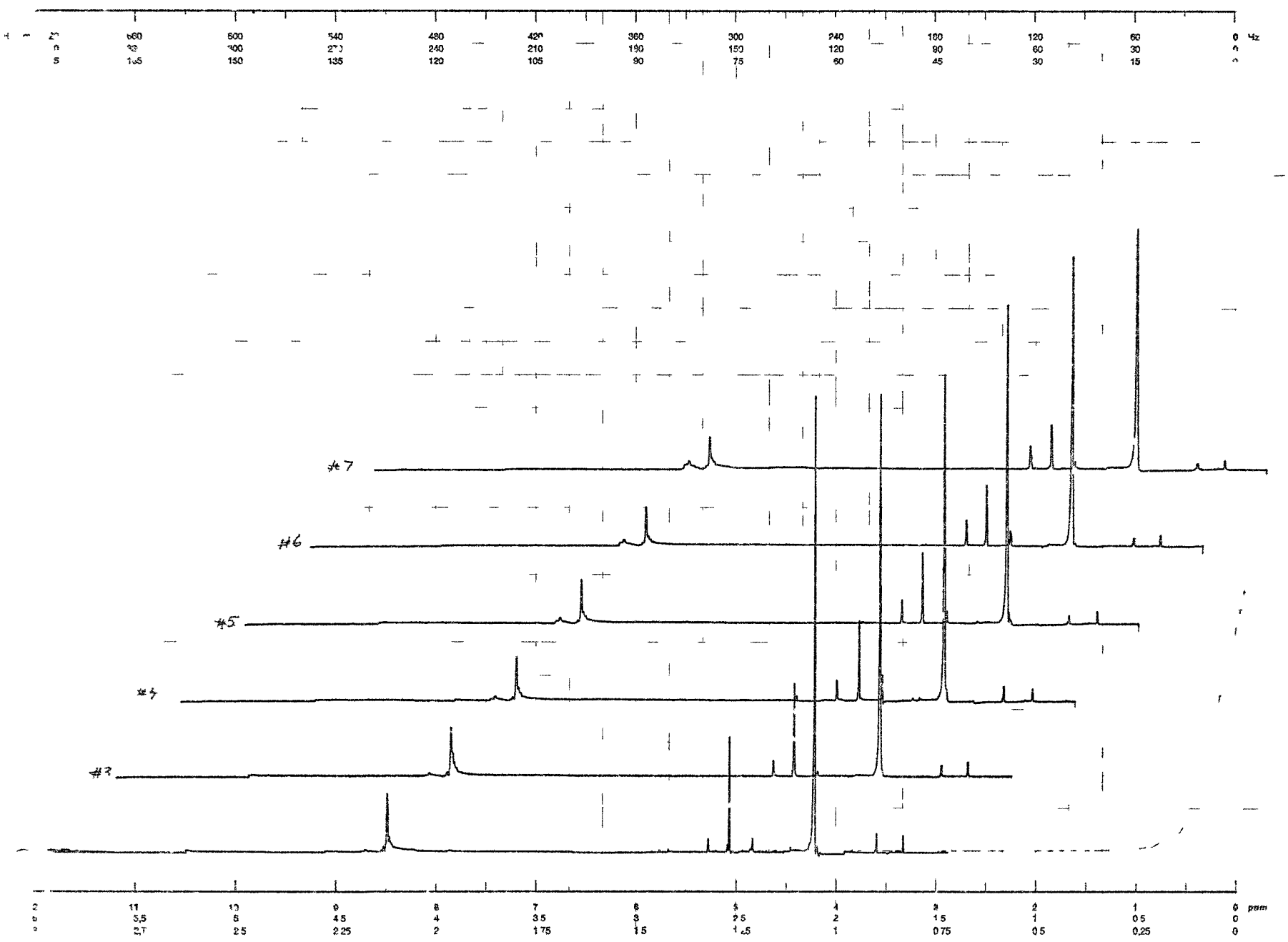
Figure A11. UV spectrum of the product of the reaction of molybdenum peroxo complex with diphenyl sulfoxide.





APPENDIX 6

Figure A12. NMR spectra of the reaction mixture of phenyl methyl sulfide, t-BuO_2H and molybdenum hexacarbonyl.



No PM-7-1/L

BRUKER
SPECTROSPIN

60 MHz - ^{1}H - Spectrum

Sample φSMe tt BuO$_2$t
Mo(CO)$_6$
Conc ___ % in CDCl$_3$
Int. Standard TMS
Temp amb ☐
333°K ☑

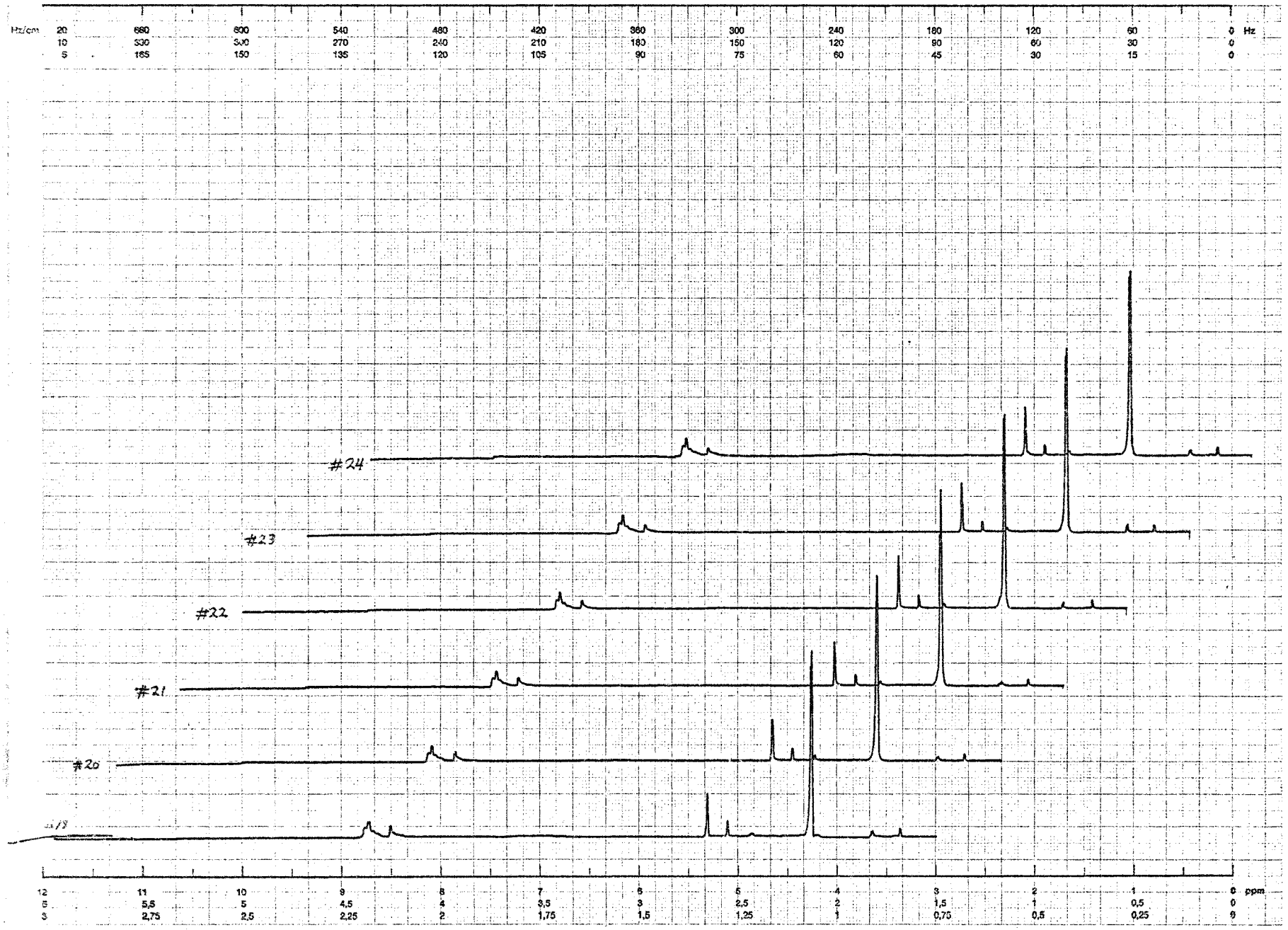
φSMe 105 M
t BuO$_2$t 20 M
Mo(CO)$_6$ not CM

Signal f_1
Pulse width (PW) 13 µsec
Points (SI) 8 K

Spectrum
width (SW) f 750 Hz/cm
Offset (A) ^{1} 2625 Hz
Time 5.5 sec
times (NS) 4 scans
Time constant (TC) —

Decoupling f_2
Frequency — Hz
Power —

Date 17/11/79
Operator SK



No [illegible]

BRUKER
SPECTROSPIN

60 MHz-^{1}H-Spectrum

Sample $\phi SMe + t\text{-}BuO_2H$
$Mo(CO)_6$
Conc. ____ % in $CDCl_3$
Int. Standard TMS
Temp. amb. ☐
303 °K ☑

ϕSMe	1.05 M
$t\text{-}BuO_2H$	2.09 M
$Mo(CO)_6$	0.0125 M

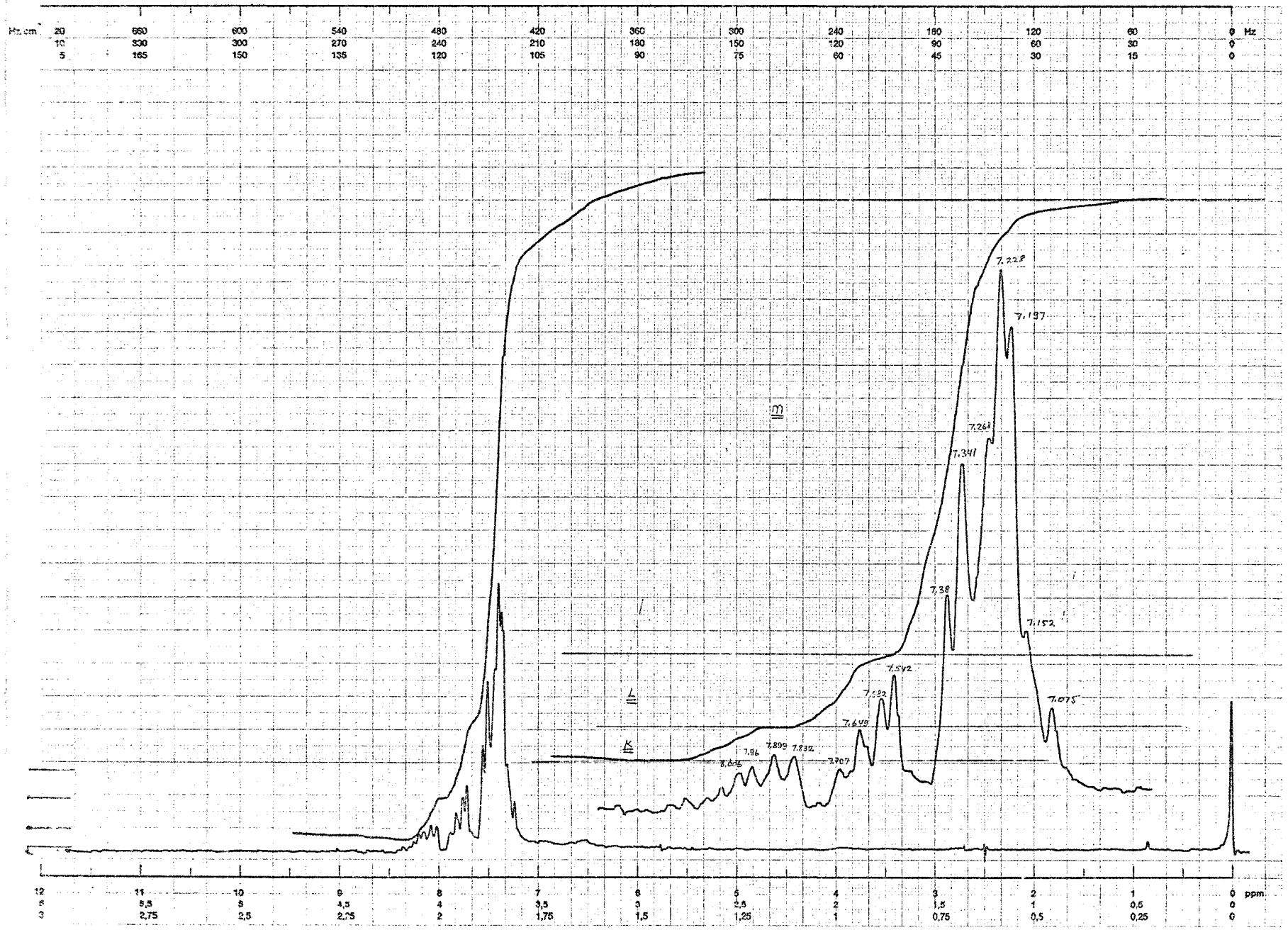
Signal f_1
Puls width (PW) 1.3 µsec
Points (SI) 8 k/ 4 k

Spectrum
width (SW) f_1 250 Hz/cm
Offset (A) f_1 2625 Hz
Time 5.5 sec
times (NS) 4 scans
Time constant (TC) —

Decoupling f_2
Frequency — Hz
Power —

Date 17/11/79
Operator S.S.K

Figure A13. NMR spectra of mixtures of diphenyl sulfide, diphenyl sulfoxide and diphenyl sulfone.



No 4/10

BRUKER
SPECTROSPIN

60 MHz - ^{1}H - Spectrum

Sample MIXTURE #2

Conc. ____ % in $CDCl_3$

Int. Standard TMS

Temp. amb. ☐

303 °K ☑

$\phi_2 S$ 1.15 ≙ 1.15M

$\phi_2 SO$ 0.998 ≙ 1.M

$\phi_2 SO_2$ 0.503 ≙ 0.5M

Signal f_1

Pule width (PW) 1.3 µsec

Points (SI) 8 k/ 4 k

Spectrum

width (SW) f_1 750 Hz/cm

Offset (A) f_1 2625 Hz

Time 5.5 sec

times (NS) 4 scans

Time constant (TC) —

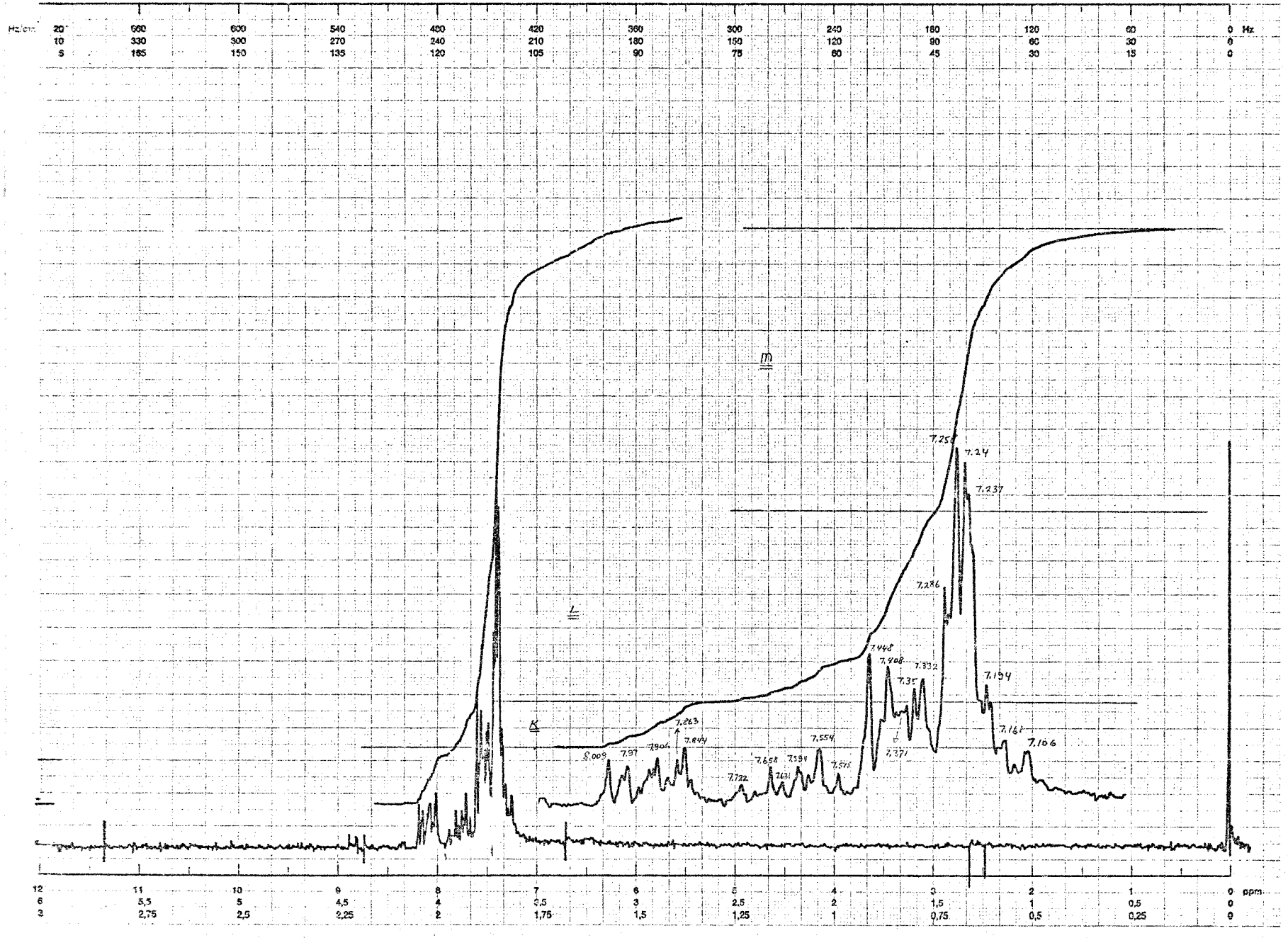
Decoupling f_2

Frequency — Hz

Power —

Date 25/11/79

Operator S.S.K



No 4/9

BRUKER
SPECTROSPIN

60 MHz - ^{1}H - Spectrum

Sample MIXTURE #1

Conc. ____ % in $CDCl_3$

Int. Standard TMS

Temp. amb. ☐

303 °K ☑

$\phi_2 S$ 0.998 ± 1 M

$\phi_2 SO$ 0.504 ± 0.5M

$\phi_2 SO_2$ 0.497 ± 0.5M

Signal f_1

Puls width (PW) 1.3 µsec

Points (SI) 8 k / 4 k

Spectrum

width (SW) f_1 750 Hz/cm

Offset (A) f_1 2625 Hz

Time 5.5 sec

times (NS) 4 scans

Time constant (TC) ____

Decoupling f_2

Frequency ____ Hz

Power ____

Date 25/11/79

Operator S.S.K

APPENDIX 7

$$Mo + H \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Mo\text{-}H$$

$$Mo\text{-}H + S \xrightarrow{k_2} SO + Mo\text{-}A$$

$$\frac{[Mo\text{-}H]}{t} = k_1[Mo]\,[H] - k_{-1}[Mo\text{-}H] - k_2[Mo\text{-}H] = 0$$

$$k_1[Mo]\,[H] - k_{-1}[Mo\text{-}H] - k_2[Mo\text{-}H]\,[S] = 0$$

$$[Mo]_o = [Mo] + [Mo\text{-}H]$$

$$[Mo] = [Mo]_o - [Mo\text{-}H]$$

$$k_1[\,[Mo]_o - [Mo\text{-}H]\,]\,[H] - k_{-1}[Mo\text{-}H] - k_2[Mo\text{-}H]\,[S] = 0$$

$$k_1[Mo]_o\,[H] - k_1[Mo\text{-}H]\,[H] - k_{-1}[Mo\text{-}H] - k_2[Mo\text{-}H]\,[S] = 0$$

$$k_1[Mo]_o\,[H] = k_1[Mo\text{-}H]\,[H] + k_{-1}[Mo\text{-}H] + k_2[Mo\text{-}H]\,[S]$$

$$k_1[Mo]_o\,[H] = [Mo\text{-}H]\,[\,k_1[H] + k_{-1} + k_2[S]\,]$$

$$[Mo\text{-}H] = \frac{k\,[Mo]_o\,[H]}{k_1[H] + k_{-1} + k_2[S]}$$

$$v = \frac{\partial[S]}{\partial t} = + \frac{\partial[SO]}{\partial t} = k_2[Mo\text{-}H]\,[S]$$

$$v = \frac{k_1 k_2 [Mo]_o\,[S]\,[H]}{k_1[H] + k_{-1} + k_2[S]}$$

$$v = \frac{k_2 [Mo]_o [S] [H]}{[K' + [H]]}$$

Where $$K' = \frac{k_1 + k_2 [s]}{k}$$

Treatment of the data according to the method of Lineweaver and Burk,

$$\frac{1}{v} = \frac{K'}{k [Mo] [S] [H]} + \frac{1}{k_2 [Mo] [S]}$$

Plotting $\frac{1}{v}$ versus $\frac{1}{[H]}$ would give K' and k_2

APPENDIX 8

ERROR CALCULATIONS.

$$I\,O_3^- + 5\,I^- + 6\,H^+ = 3\,I_2 + 3\,H_2O$$

$$3\,I_2 + 6\,S_2O_3^= = 3\,S_4O_6^= + 6\,I^-$$

$$\frac{W}{M1}\,6 = \frac{V1 * M2}{1000}$$

$$RO_2H + 2\,I^- + H^+ = I_2 + ROH + H_2O$$

$$I_2 + 2\,S_2O_3^= = S_4O_6^= + 2\,I^=$$

$$T\text{-}BUO_2H = \frac{V1 * M1 * 1000}{1000 * 2 * 0.5}$$

$$T\text{-}BUO_2H = \frac{V1 * 3 * W * 1000}{0.5 * M1 * V2}$$

$$(P) = \frac{V1 * W * 3000}{M1 * V2 * V3}$$

V1 = VOLUME $NA_2S_2O_3$ USED FOR STANDARTIZATION

W = WEIGHT OF KIO_3 WHICH IS USED IN STANDARTIZATION

M1 = MOLECULAR WEIGHT OF KIO_3

V3 = VOLUME USED FOR SAMPLING OF THE REACTION MIXTURE

V2 = VOLUME USED FOR SAMPLE (DETEMINATION OF RO_2H)

M2 = MOLECULAR WEIGHT OF $NA_2S_2O_3$

P = [T-BUOH]